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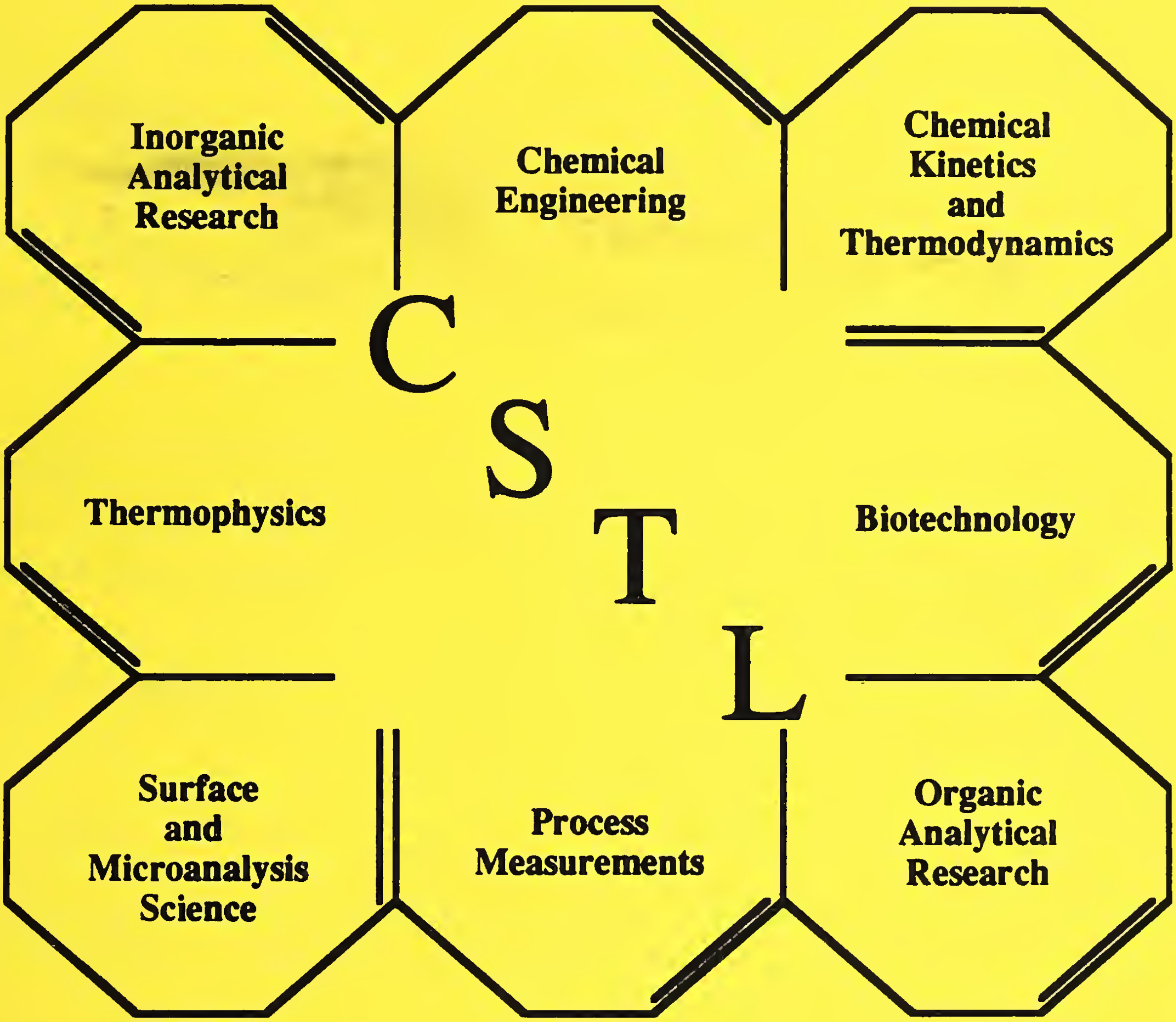
Technical Activities 1991


Inorganic Analytical Research
Chemical Engineering
Chemical Kinetics and Thermodynamics
C
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Thermophysics
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Biotechnology
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Surface and Microanalysis Science
Process Measurements
Organic Analytical Research

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology

Submitted to the Board on Assessment of NIST Programs,
National Research Council

February 11-12, 1992

Chemical Science and Technology Laboratory

1991

Technical Activities

Submitted to the Panel for
Chemical Science and Technology Laboratory
Board on Assessment of NIST Programs
National Research Council

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Harry S. Hertz, Director
Barry I. Diamondstone, Deputy Director
Chemical Science and Technology Laboratory
National Institute of Standards and Technology

U.S. DEPARTMENT OF COMMERCE, Robert A. Mosbacher, Secretary
National Institute of Standards and Technology, John W. Lyons, Director

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Glossary-List of Acronyms

γ-IFN	Gamma-interferon
2-D	2-dimensional
2D COSY	Correlation Spectroscopy Experiment in 2D NMR
830	Chemical Science and Technology Laboratory
831	Biotechnology Division
832	Chemical Engineering Division
833	Chemical Kinetics and Thermodynamics Division
834	Inorganic Analytical Research Division
835	Organic Analytical Research Division
836	Process Measurements Division
837	Surface and Microanalysis Science Division
838	Thermophysics Division
AAAR	American Association for Aerosol Research
AACC	American Association for Clinical Chemistry
ACS	American Chemical Society
ADC	Analog to Digital Converter
AEM	Analytical Electron Microscopy
AES	Auger Electron Spectroscopies
AF	Air Force
AGA	American Gas Association
AIAA	American Institute of Aeronautics and Astronautics
AIChE	American Institute of Chemical Engineers
AMES	NASA Ames Research Center
AMMTAP	Alaska Marine Mammal Tissue Archival Project
AMP	Adenosine 5'-monophosphate
AMS	Accelerator Mass Spectrometry
ANSI	American National Standards Institute
APA	Automated Particle Analysis
API	American Petroleum Institute
APS	American Physical Society
ASHRAE	American Society of Heating, Refrigeration and Air Conditioning Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ASTPHLD	Association of State and Territorial Public Health Laboratory Directors
ATO	Antimony Tin Oxide
ATPase	Adenosine Triphosphatase
AVS	American Vacuum Society
BASIC	Beginner's All-Purpose Symbolic Instruction Code
BEEM	Ballistic Electron Emission Microscopy
BMCD	Biological Macromolecule Crystallization Database
BRDC	Biotechnology Research and Development Corporation
BRS	Biotechnology Research Subcommittee

BSA	Bovine Serum Albumin
BTU	British Thermal Unit
C_{18}	Octadecylsilane
CAALS	Consortium on Automated Analytical Laboratory Systems
CAD	Collisionally-activated dissociation
CAML	Computing and Applied Mathematics Laboratory
cAMP	cyclic AMP, Adenosine 3,5-cyclic Monophosphate
CAP	College of American Pathologists
CARB	Center for Advanced Research in Biotechnology
CARS	Coherent Anti-Stokes Raman Spectroscopy
CCD	Charge Coupled Device
CCP	Cytochrome c Peroxidase
CDC	Centers for Disease Control
CE	Capillary Electrophoresis
CERT	Centre d'Etude et de Recherches de Toulouse, France
CFC	Chlorofluorocarbon
CFD	Computational Fluid Dynamics
CID	Charge Injection Device
CLSH	Committee on Life Science and Health
CNDP	Cold Neutron Depth Profiling
CRDA	Cooperative Research and Development Agreement
CSTL	Chemical Science and Technology Laboratory
CTW	Cold Tube West
CVD	Chemical Vapor Deposition
CW	Continuous Wave
DAC	Digital to Analog Converter
DARPA	Defense Advanced Research Projects Agency
DHHS	Department of Health and Human Services
DLC	Diamond Like Carbon
DMP	Dimethylphenanthrene
DNA	Deoxyribonucleic Acid
DoC	Department of Commerce
DoD	Department of Defense
DoE	Department of Energy
DoE-METC	Dept. of Energy/Morgantown Energy Technology Center
DTA	Differential Thermal Analysis
DTSA	Desktop Spectrum Analyzer
EDTA	Ethylenediaminetetraacetate
EEEL	Electronics and Electorial Engineering Laboratory
ELISA	Enzyme Linked Immunosorbant Assay
EMAP	Environmental Monitoring & Assessment Program Engineers
EMPA	Electron Microprobe Analysis
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration

FAB	Fast Atom Bombardment
FB	Fluid Bed
FBI	Federal Bureau of Investigation
FCCSET	Federal Coordinating Committee on Science, Engineering, and Technology
FDA	Food and Drug Administration
FE	Field Emission
FIIA	Flow Injection Immunoassay
FITC	Fluorescein Isothiocyanate
FPAXIAL	Fixed Point Axial Heat Flow Apparatus
FT	Fourier Transform
FTIR	Fourier Transform Infrared
FTS-ICP	Fourier Transform Spectrometry Inductively Coupled Plasma
FY	Fiscal Year
GC/MS	Gas Chromatography/Mass Spectrometry
GEC	Gaseous Electronics Conference
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GHP	Guarded Hot Plate
GITC	2,3,4,6-tetra-O-acetyl-beta-D-glucapyranosye Isothiocyanate
Goddard	NASA Goddard Space Flight Center
gpm	Gallons Per Minute
GRI	Gas Research Institute
GRT	Germanium Resistance Thermometers
HaeIII	Restriction Enzyme from Hemophilus Aegypticus
HDL	High Density Lipoprotein
HGBOC	High Boiloff Calorimeter
HPLC	High Performance Liquid Chromatography
HPOTP	High Pressure Oxygen Turbopump
HTSPRT	High-Temperature Standard Platinum Resistance Thermometer
I/O	Input/Output
IAEA	International Atomic Energy Agency
ICLASS	International Conference on Liquid Atomization and Spray Systems
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ID-TIMS	Isotope Dilution-Thermal Ionization Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IEEE	Institute for Electrical and Electronic Engineering
IFCC	International Federation of Clinical Chemistry
IgG	Immunoglobulin G
IMFP	Inelastic Mean Free Path
IMP	Inosine 5'-monophosphate
INAA	Instrumental Nuclear Activation Analysis
IR	Infrared Spectroscopy
ISA	Instrument Society of America
ISO	International Standards Organization

ISS	Ion-Scattering Spectroscopies
ITO	Indium Tin Oxide
ITS-90	International Temperature Scale of 1990
IUPAC	International Union of Pure and Applied Chemistry
IUVSTA	International Union of Vacuum Science Techniques and Applications
JPL	Jet Propulsion Laboratory
LAMMA	Laser Microprobe Mass Analyzer
Langley	NASA Langley Research Center
LANS	Low Angle Neutron Scattering
LC	Liquid Chromatography
LD_{50}	Dose which would be Lethal to One-half of the Population
LDL	Low Density Lipoprotein
LDR	Linear Dynamic Range
LDV	Laser Doppler Velocimetry
LEED	Low Energy Electron Diffraction
Lewis	NASA Lewis Research Center
LIF	Laser Induced Fluorescence
LMIS	Liquid Metal Ion Source
LNG	Liquefied Natural Gas
Lp(a)	Lipoprotein (a)
LTGHP	Low Temperature Guarded Hot Plate
MAP	Measurement Assurance Program
MAS	Microbeam Analysis Society
MBE	Molecular-Beam Epitaxy
MECE	Micellar Electrokinetic Capillary Electrophoresis
MFL	Manufacturing Engineering Laboratory
MLI	Multi-Layer Insulation
MMS	Minerals Management Service
MPI	Methylphenanthrene Concentration Ratios
MRS	Materials Research Society
MS	Mass Spectrometry
MSEL	Materials Science and Engineering Laboratory
MVMA	Motor Vehicle Manufacturers Association
MW	Molecular Weight
MW	Megawatt
NAA	Nuclear Activation Analysis
NADH	Nicotinamide Adenine Dinucleatide (reduced form)
NASA	National Aeronautics and Space Administration
NATO	North American Treaty Organization
NBSR	National Bureau of Standards Reactor
NCAR	National Center for Atmospheric Research
NCCLS	National Committee for Clinical Laboratory Standards
NCI	National Cancer Institute
NDP	Neutron Depth Profiling

NIH	National Institutes of Health
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NMMTB	National Marine Mammal Tissue Bank
NMR	Nuclear Magnetic Resonance
NMRI	Nuclear Magnetic Resonance Imager
NO	Nitric Oxide
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
NS&T	National Status and Trends
NSF	National Science Foundation
NVLAP	National Voluntary Laboratory Accreditation Program
OES	Optical Emission Spectrometry
OMB	Office of Management and Budget
OMCVD	Organometallic Chemical Vapor Deposition
ONERA	Office National d'Etude et de Recherches Aerospatiales, France
OPTR	Orifice Pulse Tube Refrigerator
OSB	Oversight Board
PAGE	Polyacrylamide Gel Electrophoresis
PAH	Polycyclic Aromatic Hydrocarbon
PAL	Programmable Array Logic
PCB	Polychlorinated Biphenyl
PCR	Polymerase Chain Reaction
PEELS	Parallel Detection Electron Energy Loss Spectrometry
PFSA	Polyperfluorosulfonic Acid
PGAA	Prompt Gamma Activation Analysis
PL	Physics Laboratory
PLM	Polarized Light Microscopy
ppb	Parts-Per-Billion
pptr	Parts-Per-Trillion
PRT	Platinum Resistance Thermometer
QA	Quality Assurance
REE	Rare Earth Elements
REMPI	Resonance Enhanced Multiphoton Ionization
RF	Radio Frequency
RFLP	Restriction Fragment Length Polymorphism
RHEED	Reflective High Energy Electron Diffraction
RIA	Radio Immunoassay
RIF	Reduction In Force
RIMS	Resonance Ionization Mass Spectrometry
RIRT	Rhodium-Iron Resistance Thermometer
RSF	Relative Sensitivity Factor
SAM	Self-Assembled Monolayer
SAXS	Small Angle X-Ray Scattering

SCF	Supercritical Fluid
SCWO	Supercritical Water Oxidation
SDIO	Strategic Defense Initiative Office
SDP	Sputter Depth Profiling
SEM	Scanning Electron Microscopy/Micrograph
SEMATECH	Semiconductor Industry Technology Consortium
SERS	Surface Enhanced Raman Spectroscopy
SES	Senior Executive Service
SFE	Supercritical Fluid Extraction
SIBFA	Sum of Interactions between Fragments Computer ab initio
SIGMA	Supersonic Inert-Gas Metal Atomization
SIMOX	Separation by Implanted Oxygen
SIMS	Secondary Ion Mass Spectrometry
SLM	Standard Laboratory Modules
SPIE	Society of Photo-Optical Instrumentation Engineers
SPRT	Standard Platinum Resistance Thermometer
SRMs	Standard Reference Materials
SSC	Superconducting Super Collider
SSME	Space Shuttle Main Engine
STEM	Scanning Transmission Electron Microscope
TADOPTR	Thermoacoustically Driven Orifice Pulse Tube Refrigerator
TANGL	Thermoacoustic Natural Gas Liquefier
TC	Thermocouple
TDLAS	Tunable Diode Laser Absorption Spectroscopy
TGA	Thermal Gravimetric Analysis
THAF	Thermally Assisted Laser Induced Fluorescence
TIMS	Thermal Ionization Mass Spectrometry
TIR	Total Internal Reflection (Spectroscopy)
TNF	Tumor Necrosis Factor
TOF-MS	Time-of-Flight-Mass Spectrometry
TRITC	Tetramethylrhodamine Isothiocyanate
TSC	Test Station Controller
UF	Ultrafiltration
USGS	US Geological Survey
UV/IR	Ultraviolet-Visible (Infrared Spectroscopy)
UV-VIS	Ultraviolet-Visible (Spectroscopy)
VAMAS	Versailles Project on Advanced Materials and Standards
VHTGHP	Very High Temperature Guarded Hot Plate
VOC	Volatile Organic Compounds
WERB	Washington Editorial Review Board
WHOI	Woods Hole Oceanographic Institution
WRDC	Wright Research and Development Center
XPS	X-Ray Photoelectron Spectroscopies
XRF	X-Ray Fluorescence Spectrometry

CHEMICAL SCIENCE
AND
TECHNOLOGY LABORATORY

Chemical Science and Technology Laboratory

Harry S. Hertz, Director
Barry I. Diamondstone, Deputy Director

A. Program Overview

The expanded responsibilities we have been given in becoming the National Institute of Standards and Technology, as reflected in our revised mission statement and enabling legislation, provide a challenge for us. We are instructed to more directly couple our research with industrial needs in the United States, while continuing to provide: the national system of chemical measurement, the fundamental research base for tomorrow's chemical science and technology, and a national reference laboratory to address critical problems related to public health and safety. With these goals in mind, the following comprehensive mission statement has been written for the Chemical Science and Technology Laboratory:

a) provide the national system of chemical measurement; coordinate the system with measurement systems of other nations and furnish essential services leading to accurate and uniform chemical measurement throughout the Nation's scientific community, industry, and commerce; provide advisory and research services to other government agencies; conduct basic and applied research in analytical chemistry, biotechnology, chemical engineering, and physical chemistry; and conduct interdisciplinary research efforts with other NIST laboratories in these areas;

b) conduct fundamental investigations of the phenomena on which measurement of the composition and behavior of chemical and biochemical systems is based; provide benchmark experimental data, new theory and models to explain the behavior and predict the properties of chemicals in chemical and biochemical processes and systems; develop and certify Standard Reference Materials; produce and evaluate Standard Reference Data; acquire and disseminate thermophysical, thermodynamic, kinetic, and thermal data; provide calibration services for temperature, pressure and vacuum, flow, volume, liquid density, and humidity; develop new laboratory and process measurement techniques, including in-situ real-time process measurement methods;

NOTE: Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

c) aid competitiveness in the global marketplace for the diverse U.S. industries that are reliant on generic research and technology development in chemistry and chemical engineering; develop and improve measurement capability and quantitative understanding of basic physical processes that underlie measurement science, including methods for analytical chemistry, biological chemistry, chemical kinetics, thermodynamics, and surface science, and thereby improve the comparability among laboratories; use the methods to assist in the solution of problems of national impact, e.g., in improving the accuracy of clinical analytical chemistry, air and water pollution analysis, and chemical engineering metrology.

Our current activities address important areas within the mission of the Chemical Science and Technology Laboratory. Two indicators of our success in meeting the expanded responsibilities of our new mission are the Cooperative Research and Development Agreements (CRDAs) executed and the patents applied for during the past year. Several highlights of the past year in these areas are described below.

By the end of FY91, CSTL scientists were involved in 19 CRDAs and had an additional 6 CRDAs pending. A large number of the current agreements involved work in the areas of biotechnology and automated analytical laboratory systems. Several of the pending agreements involve our Boulder activities in chemical engineering separation science. Patent applications are becoming a larger part of CSTL technical output. During the last FY three CSTL patents issued and there were 21 (out of a total of 70 throughout NIST) active patent inventions in CSTL. In addition, there were 11 pending patent applications from CSTL.

Through a CRDA with ICN Biomedicals, Inc., the NIST/CARB Biological Macromolecule Crystallization Database is being interfaced to crystallization robotics. Almost 1500 recipes for producing crystalline forms of over 900 biological molecules are available to the robot, allowing the easy design of crystallization experiments.

An on-going CRDA involving the College of American Pathologists has led to the issuance of four Standard Reference Materials for use in evaluating drugs of abuse in urine. The drugs include marijuana, cocaine, morphine, codeine and their metabolites. Laboratories engaged in the detection of drugs of abuse will use these SRMs to evaluate the accuracy of their methods. Two of these SRMs were issued this year. Each certified component was determined by at least two methods using GC/MS, LC/MS, or MS/MS.

A patent has been awarded recently to Dr. Terrence Jach and members of the NIST Electronics and Electrical Engineering Laboratory for a diffraction device which detects the Bragg condition. Synchrotron radiation is currently our most intense continuous source of x-ray energy. Synchrotron light sources are extensively used for materials research, for x-ray lithography in the semiconductor industry, for protein crystallography, and for medical angiography. Most of these technological applications require a monochromatic source of x-rays, produced by diffracting the radiation twice from crystals or gratings. A complicated mechanical or electronic stabilization system is required to keep the two diffracting elements properly aligned. The invention facilitates this alignment enormously by the use of an x-ray detector that is integrated into a semiconductor crystal which is simultaneously used as the diffracting element and the detector. The electrical signal generated by the proper alignment of the crystal is used in a feedback loop which operates continuously. There are currently several synchrotron light sources in every industrialized country, each with 30-100 beamlines requiring monochromators. It is expected that the application of this invention will be widespread.

A patent application has been filed by Dr. Kenneth Kreider for corrosion resistant thin-film thermocouples. The two legs of the thermocouple are made of ruthenium oxide and iridium oxide. These two materials are excellent electrical conductors with high resistance to corrosion and the resulting sensor has a response time as fast as 1 μsec. This thermocouple will enable the continuing miniaturization of sensors and electrodes.

While industrial competitiveness and industrial collaborations are extremely important, the vitality of our Laboratory is still very dependent on an outstanding research base. During the past year we have initiated an extremely exciting program to focus cold neutrons, with the goal of improving detection limits for quantitative analysis techniques such as neutron depth profiling and prompt gamma activation analysis. Using the flexibility of ultrathin single crystal silicon wafers to form a system of curved totally reflecting mirrors is one avenue that is being investigated. In addition, a cooperative research project is underway with researchers at the State University of New York and Nalchek University in Russia to develop an optics system based on the use of hundreds of hollow capillary tubes to focus neutrons. We have already succeeded in some focusing and bending of neutron beams using this latter approach!

Our "classical" services to industry are still very strong and very important. In the health area, I have already mentioned our new drugs-of-abuse in urine SRMs and a new human serum SRM also has been issued. During the past year several significant new Standard Reference Databases were released. The Structures and Properties Database allows the user to draw the structure of a target molecule on a computer screen and the program then generates estimated values for heat of formation, vapor pressure, and boiling point. The program also allows the user to create a balanced chemical reaction and computes the equilibrium constant between 300 and 1500 K.

Many important industrial processes and research activities occur in the transition pressure range. In this range, typically 0.1 to 10 Pa, gas dynamics change from being dominated by molecule-molecule collisions to molecule-gas collisions. This transition can affect vacuum gauges in significant ways and also places fundamental constraints on the construction of a vacuum standard. A new primary vacuum standard to cover the range of 10^{-4} to 10^{2} Pa has been built. It will allow the calibration of both spinning rotor gauges and low-range capacitance manometer gauges. This standard will not only allow the exploration of significant gauge non-linearities, but will bridge the gap between the high vacuum and low pressure primary standards.

As this overview indicates, we strive to achieve a balance between the provision of currently needed measurements and technology, and more basic research to ensure a healthy science and technology base for the future. Each Division in the Laboratory is responsible for basic and applied research, and for maintaining close contacts with appropriate scientific and user communities.

In the following pages, recent activities, technical directions and outputs of the CSTL Divisions are highlighted.

B. Outputs and Interactions (Chemical Science and Technology Program)

1. Talks

Hertz, H.S., "Chemistry Opportunities in Federal Agencies," The Association of College and University Offices, Inc., DuPont Plaza Hotel, Washington, DC, March 25, 1991

Hertz, H.S., "Quality in Environmental Characterization and Measurements: The Asbestos Success Story?", Workshop on Environmental Chemistry -- Board on Chemical Sciences and Technology (BSCT), Washington, DC, May 6, 1991

Hertz, H.S., "Accuracy and Quality Assurance in the Analytical Laboratory," Analytical Laboratory Managers Association, NIST Gaithersburg, MD, October 23, 1991

2. Committee Assignments

B.I. Diamondstone

American Chemical Society
Committee on Chemical and Public Affairs
    Subcommittee on Research and Science Policy
ASTM Committee D34, Hazardous Wastes
ASTM Committee E-01, Chemical Analysis of Metals
ASTM Committee E01.01, Ferrous Metals
ASTM Committee E01.20, Fundamental Practices (Secretary)
Task Group on Oxygen in Metals (Chairman)
Analytical Laboratory Managers Association (President-Elect)
Member, Council for Chemical Research

H.S. Hertz

Nominating Committee, American Society for Mass Spectrometry (Chairman)
ASTM, Committee D19 on Water
ASTM, Committee E48 on Biotechnology
Public Relations Committee, Council for Chemical Research
Directors of Industrial Research - Analytical Group
Analytical Laboratory Managers' Association
National Reference System for the Clinical Laboratory, NCCLS (Chairman)
Editorial Advisory Board, Chemical and Engineering News
Advisory Committee for the 1992 Power of Quality Conference
Standards Committee - American Association for Clinical Chemistry
Standards Committee - College of American Pathologists (Consultant)
NCCLS Strategic Planning Task Force

3. Laboratory Colloquium Series

March 27, 1991

Dr. Stephen Scharf, Research Associate, Cetus Corporation, Emeryville, CA, "The Polymerase Chain Reaction: How You Can Use PCR for Everything from Cloning Your Genes to Figuring Out Whodunit"

June 12, 1991

Dr. Thomas Poulos, Director of CARB, Rockville, MD, "Structural Aspects of Enzyme Catalyzed Peroxide/02 Activation and Interprotein Electron Transfer"

July 10, 1991

Dr. Mike Kurylo, NIST, Gaithersburg, MD, "Present State of Chemical Knowledge of the Upper Atmosphere"

BIOTECHNOLOGY

I. Biotechnology Division (831)

Lura J. Powell, Chief

A. Division Overview

The NIST Biotechnology Division is a new organization created as a part of an agency-wide reorganization in February, 1991. Scientists from seven technical divisions were brought together to form the new division which brings to fruition an effort begun in the mid-1980's to establish a major new NIST effort to develop the generic measurements, models, data and standards needed to accelerate the commercialization of biotechnology in the United States.

At the behest of the U.S. Senate, NIST prepared a plan for a national effort to develop measurements and standards for biotechnology. The plan recognized that commercialization of biotechnology will be measurement intensive with an estimated cost of up to 25 percent added to the products of biotechnology for such measurements. Measurements are vital in each developmental stage of a biochemical product--in the research laboratory, in the proof of process and process equipment scale-up in pilot plants, in commercial scale production, and in assuring that products meet or exceed market standards and customer specifications. These measurements are primarily chemical and physical in nature.

The development of the NIST Biotechnology program was initiated and expanded through support of the Director's Competence Fund, a program that provides seed money, over a period of up to five years, for NIST to develop scientific and technical competence in a new area. Efforts were initiated in bioanalytical separations, sensor technologies, biophysical chemistry, structural biology, and bioprocess engineering. Because of the interdisciplinary nature of biotechnology, competence funding and appropriations were obtained to support activities in several major organizational units at NIST. A serious funding issue for the NIST Biotechnology program currently exists because of the expiration of several competence projects in FY92.

The new Biotechnology Division provides NIST with a cohesive biotechnology effort focussed on the most critical measurement needs of the biotechnology industry, fosters collaboration among NIST scientists conducting biotechnology research, and raises the visibility of NIST contributions to biotechnology research, standards and data leading to collaborations with industry, universities and other government agencies. Word spread quickly that NIST had a Biotechnology Division, and a number of companies have visited the division and found areas for proposed collaboration. One of the most difficult issues associated with the creation of the division was the proposed transfer of five staff members from the Boulder lab. Unfortunately only one of the five staff members elected to transfer to the Gaithersburg site. Since most of those staff members were chemical engineers associated with the bioprocess separations program, the division is faced with the challenge of replacing them and building a strong bioprocess engineering effort.

Visibility of the NIST Biotechnology Division was further enhanced when the Federal Coordinating Committee on Science, Engineering, and Technology (FCCSET) under the leadership of the President's Science Advisor, Dr. D. Allan Bromley, in cooperation with the Office of Management and Budget (OMB), selected biotechnology research as a budget cross-cut for FY93. The Biotechnology Research Subcommittee (BRS) of the FCCSET Committee on Life Science and Health (CLSH) was given primary responsibility for developing an inventory of biotechnology research throughout the Federal government and providing recommendations on areas of opportunity for the future. Personnel of the NIST Biotechnology Division serve on the bioprocessing, structural biology, health, general/foundations and infrastructure Working Groups of the BRS which evaluated the Agency submissions and provided recommendations to the BRS Committee. As a result of this involvement, the NIST Biotechnology program, although representing only 0.1% of the total Federal investment in biotechnology research, is well represented in the cross-cut recommendations and a number of collaborations have been initiated with other agencies.

The Division is participating in a National Research Council Study on Bioprocess Engineering. The study will examine research priorities and policy issues in bioprocess engineering of relevance to both specialty, high-value products (e.g., therapeutic drugs) and commodity, low-value chemical products (e.g., liquid fuels). It will focus on the opportunities and needs of bioprocess engineering with particular emphasis on the interface of biology and engineering and will identify major areas of research and development for the next decade. Involvement in this study will provide visibility for the NIST Biotechnology program and will assure that the importance of measurement research, standards, and data will be recognized.

The mission of the NIST Biotechnology program is to advance the commercialization of biotechnology by developing the scientific/engineering technical base, reliable measurement techniques and data to enable U.S. industry to quickly and economically produce biochemical products with appropriate quality control. As with all NIST programs, a major emphasis of the NIST biotechnology program is to provide advisory and research services to industry, other government agencies and the scientific community. The Division was initially organized into three groups, (1) Biochemical Measurements whose activities are focussed on separation, modification, immobilization and stabilization of biomolecules, and the development of biosensor technology; (2) Biophysical Measurements, whose activities focus on biothermodynamics, transport processes of biomolecules, mechanisms of DNA damage and repair, and membrane dynamics; and (3) Center for Advanced Research in Biotechnology (CARB), whose activities focus on the understanding of protein structure/function and energetics. CARB is a joint venture with the University of Maryland and Montgomery County, Maryland. An outstanding facility with sophisticated state-of-the-art instrumentation, CARB provides an exceptional environment for training graduate students and postdoctoral fellows in fields critical to the future of biotechnology. The primary research efforts at NIST are focused on:

DNA and Protein Chemistry/ Standards Development

DNA Profiling: Methods and standards are being developed to accurately characterize DNA profiles for forensic and other uses. A standard reference material for quality control and standardization of forensic DNA testing is being prepared for release early in 1992. Research is being conducted to develop the next generation of DNA profiling based on polymerase chain reaction (PCR) technology including new methods development for rapid DNA extraction, amplification, separation, and computer imaging.

DNA Damage and Repair: Methods have been developed to characterize DNA damage on a molecular scale using GC/MS techniques. Studies of both *in-vivo* and *in-vitro* systems are underway to understand both damage (as low as one base per million) and repair mechanisms.

Protein Mapping: 2-D electrophoresis, computer imaging and computational techniques are being applied to mapping of proteins in complex systems, including those of living tissues subjected to disease and treatments.

Bioprocess Engineering

Sensor Technologies: NIST develops generic sensor technologies useful for the measurement of specific analytes in bioreactors and in living tissue, and also for the measurement of "bulk properties" such as temperature and pH in bioreactors.

Separation and Purification: Methodologies and the data necessary for their evaluation are being developed to effect the efficient separation and purification of products from their mother liquors.

Design Properties: Thermophysical, thermochemical and engineering properties are being obtained, evaluated, codified and modelled for ubiquitous biochemicals, protein solutions, and chromatographic media of interest to biotechnology. These data will be used by the bioengineer to both optimize existing processes and to evaluate proposed processes.

Protein Engineering (Structural Biology)

Structure/Function/Energetics Relationships: NIST is actively working to understand these relationships using the methods of protein crystallography, molecular biology, biothermodynamics, and computational chemistry and modelling.

Protein Crystallography: Active programs are underway to obtain the protein structure, using X-ray and NMR techniques of prototypical proteins, enzymes, enzyme-substrate complexes and model DNA systems. Other efforts include the development of a machine readable database for protein crystallization and the development of artificial intelligence techniques for interfacing laboratory robots for protein crystallization studies with the database.

Protein Folding: Computational and experimental methods have been developed to determine the thermodynamics, cooperativity and other parameters describing the energetics of protein folding.

Computational Chemistry and Modelling: Quantum mechanical formalisms involving reaction fields are being developed to model the energetics and dynamics of interactions between substrates and active sites of enzymes. Modelling techniques to understand the relationship between protein sequence and structure are being developed.

In spite of changes associated with the reorganization at mid-year, the staff was highly productive. Research efforts in the Division resulted in 101 articles published or in press. Division scientists also presented more than 90 talks at technical meetings and conferences.

Two members of the Division, Dr. Dennis Reeder and Dr. Anne Plant were selected to receive Department of Commerce Medal Awards. Dr. Reeder received the Department of Commerce Silver Medal for "outstanding contributions to the development and application of methods for the separation of complex mixtures of biomolecules". Dr. Plant, jointly with Laurie Brown of Division 835, received the Department of Commerce Bronze Medal for "outstanding efforts and unusual creativity in the conception, development and critical evaluation of a prototype Liposome-based Flow Injection Immunoassay measurement device." Dr. Lura Powell received the 1991 Outstanding Public Service Award from the Montgomery County Chapter of the International Personnel Management Association for creativity in resolving personnel issues and for leadership in the establishment of a child care center at NIST.

Future Directions

Future thrusts of the NIST program include expanded DNA separations and biosensor technology efforts, providing quality assurance measurements and standards for industrial applications and the human genome project, and new programs in biomolecular electronics, biomimetic chemistry and the spectroscopic studies of biomolecular systems. Plans have been developed for program expansions in biosensor technology, bioprocess engineering, structural biology, and measurement quality assurance. In addition plans were developed for a major NIST-wide NMR facility. These plans fit well with the recommendations of the FCCSET Biotechnology Crosscut.

Plans are underway to expand the CARB facility in cooperation with the University of Maryland. The current CARB facility is filled to capacity and plans are underway for expansion of the facility. The CARB facility is 38,000 square feet, which includes 18,000 of research space and 20,000 of conference facilities and office/administrative space. The proposed expansion, CARBIB would provide an additional 60,000-100,000 square feet for laboratory, office and teaching facilities, and space for 20-25 additional tenure-track faculty. Proposed areas of research for CARBIB include a Center for Excellence in Computational Biotechnology, synthetic and peptide chemistry, biomolecular electronics, advanced NMR measurement technology and enzymology.

B. Selected Technical Reports (Biotechnology Division)

1. Characterization of a Prototype DNA Standard Restriction Length Polymorphism Set

D.J. Reeder and K.L. Richie

Work on DNA standards was initiated in 1988. The first year was spent in a ramp-up mode, learning the technology, acquiring equipment, and networking with the DNA community to assess needs. The second year focused on evaluating potential standard DNA materials that were commercially available. Work during this past year brought the mastery of many techniques into a program centered on finalizing an appropriate DNA standard set.

We selected a set of materials best suited for a prototype standard reference material quality assurance set. The set consisted of the following: A) a molecular size ladder to accurately size DNA fragments; B) a female cell line (K562) consisting of a cell pellet to be extracted and cut with the restriction enzyme, HaeIII; genomic DNA to be cut with HaeIII; genomic DNA pre-cut with HaeIII; C) a male cell line consisting of a cell pellet to be extracted and cut with HaeIII; genomic DNA to be cut with HaeIII; genomic DNA pre-cut with HaeIII; D) a visual ladder for electrophoresis quality assurance; and E) a human DNA quantitative DNA standard set.

The standards set was sent for testing to approximately 20 forensic laboratories, including laboratories with specialties in paternity testing. The interlaboratory results were well within a 5% range of values. The results of this testing were presented at the 2nd International Conference on Human Identification and have been published.

Materials for the final configured DNA SRM have been procured, and the SRM will be qualified and certified for release in early 1992. This standard set will be used by forensic laboratories in their quality assurance programs for DNA profiling.

2. Rapid Methods for DNA Profiling in Human Identification Based on Polymerase Chain Reaction

M.C. Kline and D.J. Reeder

In the past year we concentrated our efforts on the optimization of the polymerase chain reaction (PCR) conditions for enhanced speed and increased specificity. The region of human chromosome 2 known to contain the Apo-lipoprotein B gene has several DNA regions of interest that can be amplified using appropriate DNA primers that flank the specified region.

We have optimized the conditions for DNA amplification. The previous procedure, which required six hours to complete the amplification step and 1 μg of genomic DNA produced large quantities of non-specific amplification products. The optimized procedure can be completed in 2 hrs, requires 0.3 μg genomic DNA or less, and yields specific DNA amplification products. This reduction in amplification time and increase in specificity has allowed us to amplify and evaluate the PCR products in a single day.

The second focus of our research has been the optimization of the separation of PCR products by polyacrylamide gel electrophoresis. This work has led to the ability to separate and visualize 8-13 DNA base pair differences in genetic allele sizes. By use of a moving-boundary electrophoretic system, we have been able to separate DNA alleles differing in approximately 8 base pairs in the size range of 700 - 900 base pairs.

This work is expected to have a significant impact on standardization of these newer and more efficient methods of DNA analysis. As forensic laboratories adopt PCR techniques, our research will enable us to provide timely methods and standards. During the coming year we will extend this work to optimize an assortment of highly variable genetic systems for human identification.

3. Protein Expression in Cancer Cells Treated with Chemotherapeutic Agents: Analysis by Two-Dimensional Electrophoresis and Imaging Processing

J. Edwards

Molecular events which occur during progression of normal cells to cells exhibiting neoplastic characteristics are of fundamental importance to our understanding of human cancer. The malignant transformation of human cells can be followed by the expression of proteins and other cellular metabolites that differ qualitatively and quantitatively from normal. Newly expressed proteins, or ones that are expressed at significantly higher than normal levels, may be considered tumor markers that are genetic products directly linked to the phenotype of the transformed cell. Identification and analysis of these molecular events are essential to the understanding of human cancer processes. We have used 2-D PAGE and computerized image processing to map and characterize the *in vitro* protein expression of human melanoma cells following treatment with the cytokines gamma-interferon (γ-IFN) and tumor necrosis factor (α-TNF). These factors, which are known antiproliferative agents, induced the synthesis of new proteins while also modulating the level of expression of others. We have documented altered cytokeratin expressions, modulated ras p21 protein expression and changes in the expression of tropomyosin proteins. Also, data characterizing cellular growth patterns and protein expression has been documented, and numerous tumor associated proteins have been identified.

Continuation of these studies will focus on: (1) the development of a computerized database for proteins directly associated with malignant phenotypes, and (2) assessing the value of the techniques as a tool for screening chemotherapeutic agents.

4. Confirmation of a New Amino Acid in the Siderophore Expressed by *Pseudomonas fluorescens* 244

D. Hancock

The structure elucidation of pyoverdine Pf 244, the siderophore expressed by *Pseudomonas fluorescens* 244 which, when it is grown in an iron-poor medium, has revealed the presence of a new amino acid never before reported as naturally occurring. NMR and mass spectral analyses of this pyoverdine and the N-15 labeled pyoverdine suggested the presence of ß-hydroxyhistidine as one of the six amino acids in the peptide. The *erythro*-isomer of this amino acid had been previously synthesized, and a few mg of the pure material was provided by Prof. Sidney Hecht (University of Virginia). Amino acid analysis confirmed that the *erythro*-isomer was not the amino acid in question. Prof. Hecht also provided the spent mother liquors from the late 1970's synthesis, which at the time was known to contain the *threo*-isomer as a contaminant. Approximately one mg each of residual *erythro*-and *threo*-ß-hydroxyhistidine were recovered from these mother liquors; amino acid analysis confirmed the presence of the *threo*-isomer in our pyoverdine. Chiral determination of the amino acid relied on reactions with D- and L- amino acid oxidases and subsequent amino acid analyses after derivatization with the chiral reagent GITC. This established that the pyoverdine contained L-*threo*-ß-hydroxyhistidine.

Although the *erythro*-ß-hydroxyhistidine has previously been found as a bacterial product, this is the first report of the natural occurrence of the *threo*-isomer. What makes this finding even more significant is the fact that it appears that the *threo*-ß-hydroxyhistidine serves as one of the binding groups in this iron-binding chelator. This new amino acid may prove significant in continuing efforts to synthesize new classes of iron-chelating drugs.

5. Optical Techniques for in situ Measurements of Bioprocesses

J.J. Horvath and S.A. Glazier

Recently developed biochemical and genetically engineered processes for production of new drugs and chemicals require new measurement capabilities for use in bioreactors. Most monitoring techniques rely on off-line sampling with the inherent problems of contamination, long analysis time and poor reproducibility. These problems are best avoided using nonintrusive, in-situ measurement methods, with optical techniques providing the best potential for making rapid and selective measurements. Several optical techniques such as absorption, scattering and turbidity have been investigated with various degrees of success, but none have shown the sensitivity and dynamic range required for measurements in fermentation cultures.

Fluorescence techniques have been developed for real-time, in-situ measurement of cell mass, product mass and other parameters in biochemical systems. A sensor has been developed for use inside a fermentor that consists of an optical rod that is connected by fiber optics to a fluorometer. This system is used to generate excitation wavelengths and measurements of the fluorescence spectra. Initial studies utilized the yeast *Saccharomyces cerevisiae* in a non-fluorescent medium. The fluorescence species monitored by the optical rod, in-situ, were yeast, NADH (metabolic component), and pyridoxine (product-vitamin B_6). Excitation and emission wavelengths were determined experimentally using pure solutions of the species produced in the fermentations. Fermentation fluorescence yeast growth profiles accurately tracked the dry cell mass throughout the entire fermentation to a final cell mass of 4.5 g/L. Pyridoxine fluorescence also tracked the cell mass and was a sensitive method for monitoring cell growth. The fluorescence from NADH was an unreliable measure of cell mass, due to its sensitivity to the levels of glucose and dissolved oxygen. These results are relevant to the interpretation of the signal from commercial monitors of fluorescence.

Tetracycline, an antibiotic, fluoresces when complexed by alkaline earth ions in media similar to that used in current pharmaceutical fermentations. In fermentations of *S. aureofaciens*, in synthetic non-fluorescent media, the tetracycline fluorescence measured by the optical rod sensor was linear with tetracycline concentration, as determined by a microbial bioassay.

Results indicate that tetracycline fluorescence can be measured in the presence of many industrial fermentation components. With judicious choice of excitation and monitoring wave lengths, the tetracycline fluorescence can be used to monitor its production in industrial pharmaceutical fermentions. Future work will demonstrate this in a 2.5 one laboratory fermentor. Exploratory programs on use of neural net computing for analysis of the fluorescence from the optical rod sensor and the use of Surface Enhanced Raman Spectroscopy (SERS) for monitoring proteins have provided good results.

6. Fiber Optic Glucose Sensor Based on Polymer Swelling in Polymer Gels

M. McCurley and J.R. Sachs

A new type of fiber optic biosensor based on polymer swelling coupled to optical displacement measurement was investigated. The sensing element is a crosslinked polymer which changes size as a function of analyte concentration. The polymer gel is coupled to a reflecting element such that changes in the polymer gel size causes variations in the reflector position. As the reflector position changes, the intensity of light reflected into an optical fiber varies. This change is related to analyte concentration. Fiber optic biosensors based on polymer swelling offer several potential advantages over the conventional immobilized indicator sensors reported to date. They can be designed so that the optical measurement, which is separated from the polymer by a diaphragm can not be affected by the optical properties of the sample. Unlike fiber optic sensors based on indicator absorbance or luminescence, photodegradation is not a potential source of sensor instability. Measurements can be made in the near infrared region of the spectrum and take advantage of inexpensive components available for fiber optic communications. The viability of this concept was demonstrated by a fiber optic, chemical sensor that can discriminate between alcohols such as ethanol and methanol and polar organic solvents such as toluene. The membrane is a lightly crosslinked poly(vinyl alcohol) hydrogel. A membrane for use in a glucose biosensor based on this approach was also developed. The polymer gel was prepared by immobilizing glucose oxidase in an amine-containing acrylate polymer hydrogel. The enzyme catalyzes the oxidation of glucose to gluconic acid, which protonates the amine. Electrostatic repulsion between charged amine groups causes the gel to expand. The polymer gel changes size as a function of glucose concentration in the physiological range.

A mathematical model of swelling and transport in fiber optic chemical sensors and electrically regulated separation membranes is being developed. These applications are at the forefront of chemical technology and take advantage of the same physical phenomena in polymer gels: the coupling of electric fields, transport, and chemical and mechanical kinetics. Previous models were one-dimensional and considered only very simple reaction schemes. This work will extend the model to three dimensions, and will consider more general reaction kinetics. In addition to its use in optimizing the performance of the sensor and separation systems, this model also has numerous applications in biomechanics and photographic science.

This work demonstrates a new, generic approach to optical sensing which does not depend on photoexcitation of a dye at a specific wavelength. It is anticipated that it will lead to a family of sensors that are both inexpensive and rugged, with applications in the clinical field, environmental monitoring and process control.

7. Characterization of Adsorbed Protein Layers on Thin Nylon Films: Fluorescence Energy Transfer

E.S. Grabbe

As part of our overall effort in the development and analysis of biosensors, we have employed our total internal reflection fluorescence (TIRF) system to characterize a model system consisting of layers of adsorbed immunoglobulin G (IgG) on thin nylon films. Nonspecific adsorption of proteins to nylon limits the sensitivity of sensors using nylon as a support material. In order to understand both the mechanisms behind protein adsorption and the conditions that are important in controlling adsorption, fluorescence energy transfer measurements were recorded between 1) adsorbed fluorescein isothiocyanate (FITC) tagged IgG and tetramethylrhodamine isothiocyanate (TRITC) tagged nylon, and 2) FITC labelled IgG and TRITC labelled antigen. The two energy transfer experiments characterized both the nylon/IgG and IgG/solution interfaces, respectively. Results were correlated with IgG coverage measured by the bicinchoninic acid (BCA) method and antigen binding activity assessed using TRITC-tagged antigens. The behavior of the adsorbed IgG layer was evaluated as a function of the washing buffer pH.

Two different surface layers resulted from washing with phosphate or carbonate buffers. When phosphate buffer, pH 7, was used to wash excess IgG from the nylon, IgG coverage increased with adsorption solution concentration of IgG, generating an isotherm that could be fit to a two layer model. Loss of FITC emission diminished at higher coverage while TRITC gain remained constant, supporting an IgG bilayer model, where the upper layer was no longer interacting with the TRITC labelled surface. Calculated separation distances also supported this model. Antigen incubation studies under these washing conditions revealed that the antigen both bound to and exchanged with the loosely adsorbed IgG layers. After pH 9 carbonate washes, only a tightly adsorbed, unexchangeable layer of IgG remained on the nylon surface, corresponding to less than a monolayer by coverage measurements. In a pH 9 buffer, no energy transfer took place between the FITC labelled IgG and the TRITC tagged antigen, although antigen was present on the surface after incubation, suggesting co-adsorption of antigen. When the buffer was switched to pH 7, phosphate buffer, energy transfer was observed, indicating that now binding had occurred between the antigen and antibody. These results demonstrated the utility of TIRF to monitor protein film behavior.

Exploiting new methods, such as TIRF with energy transfer to monitor changes at surface/protein interfaces, should assist future biosensor development by answering fundamental questions about how immobilization techniques effect protein conformation, how protein layers change with age of sensors, and how operating conditions alter the interfacial structure.

8. Carbohydrate-Protein Interactions: Thermodynamic Studies

D.H. Atha

Heparin is a heterogeneous sulfated polysaccharide that is widely used as an effective anticoagulant. It functions by binding antithrombin and accelerating the rate at which this protease inhibitor inactivates the proteolytic enzymes of the blood clotting mechanism. However, its clinical use is sometimes associated with bleeding. Recent studies using low molecular weight heparin fractions with high and low affinity to antithrombin, suggest that is possible to separate the antithrombotic properties from the hemorrhagic side effects. It is thus necessary to characterize the specific chemical interactions that occur between heparin and antithrombin so that more effective preparations of heparin can be designed. Thermodynamic analysis allows a complete quantification of these associations.

In collaboration with F. Schwarz, we have used titration calorimetry to determine the binding enthalpy and entropy of selected heparin fragments which vary in the location of specific sulfate groups. This is an aid in identifying the structures in heparin that are necessary for activity. In addition, commercial preparations of heparin contain impurities such as chondroitin sulfate. FDA regulations require that these impurities be kept at minimal levels. To structurally characterize and maintain uniformity of these preparations requires many analytical methods such as NMR and mass spectrometry. We have found light scattering to be a useful addition to these methods. In collaboration with A. Gaigalas, R. LeSage and J. Hubbard, we have examined the quasielastic and electrophoretic light scattering properties of commercial preparations of heparin. These data yield diffusion and mobility constants that are useful in characterizing the size and charge heterogeneity of the heparin preparations. We will use these criteria in selecting a commercial source of heparin for use as a standard reference material.

9. Biomembranes and Immunoreactions

A. Plant

Of importance to many areas of biotechnology is the interaction of macromolecules at surfaces. The physical biochemistry of macromolecular interactions at surfaces has been studied in order to understand phenomena such as the effect of multivalent interactions on rates and free energy of binding. One experimental system that has been used is liposomes, which are submicroscopic spherical structures of phospholipid bilayers that serve as model cell membranes. Liposomes can be derivatized with immunochemically active moieties such as antigens, and are readily detectable by light scattering or by the fluorescence of dyes associated with them. Previous work from this lab has shown the usefulness of liposomes as an analytical reagent in a clinical immunoassay for theophylline. Among the advantages demonstrated is the ability to engineer liposomes with varying antigen valency, and in the process, affect their binding to immobilized antibodies. We have shown that increasing the numbers of antigens in the membranes of liposomes increases their binding constants for immobilized antibodies and decreases their dissociation rate constants.

To further the use of liposomes as both an analytical tool and as a model system for multivalent binding, a collaboration was established with a group at the Gesellschaft fur Biotechnologische Forschung in Braunschweig, Germany, where a month was spent on the development of a liposome-based analytical system for the pesticide atrazine. Surface immobilized, anti-atrazine monoclonal antibodies and liposomes derivatized with atrazine will be used to understand the thermodynamic origin of increased binding strength to surfaces due to multiple points of interaction. To facilitate this study, we have been designing a continuous flow system containing immobilized anti-atrazine antibodies which will allow us to collect precise retention data of liposomes as a function of multivalency, and to determine the temperature dependence of kinetics and equilibrium parameters from these data. This experimental approach will result in a generic method, which uses small amounts of immunochemicals for rapid and precise measurement of affinity constants for antibodies. It will also impact on generic topics such as chemically specific and non-specific adsorption of macromolecules to surfaces.

Another immunoassay project, which is ongoing in collaboration with the Organic Analytical Research Division and a local medical supply company, also involves the use of continuous flow and immobilized antibodies. The goal is to develop an automatable immunoanalysis system for lipoprotein cholesterol quantitation. Immobilized antibodies specific for the lipoprotein Lp(a) will selectively remove Lp(a) particles, but not other lipoproteins, from serum. The trapped lipoprotein particles will then be subjected to on-line enzymatic quantitation of associated cholesterol.

10. The Chemistry and NMR Spectroscopy of Cyclobutanetetraone Phenylhydrazones and Anilides Derived from Squaric Acid

B. Coxon, A.J. Fatiadi, H.El Khadem, and M.A. Shalaby (American University)

Compounds in the squaric acid-semisquaric acid series are of considerable synthetic, theoretical, spectroscopic, and biological interest. For example, semisquaric acid is produced by the mold *Fusarium moniliforme*, which has been isolated from corn seed damaged by southern leaf blight. This compound has growth-regulating and phytotoxic effects on plants and a toxic effect on animals (liver damage and/or esophageal cancer when fed with corn contaminated by the mold). Herbicidal effects of squaric acid and semisquaric acid derivatives have been demonstrated, and the anomalous Raman intensities of squaric acid dianion have been thoroughly studied.

In a collaborative project with American University, reactions of squaric acid or its esters with phenylhydrazine or its derivatives have yielded a series of highly colored polyphenylhydrazones, anilides, and mixed aniline-phenylhydrazine derivatives whose structures have been studied by physical and chemical methods.

Inspection of the structures of the products reveals striking resemblances to the structures of osazones that are formed from sugars. The major products isolated in both reactions are not derivatives of the substrates, but of their oxidation products, leading to polyhydrazones of cyclobutanetetraone and of osuloses, respectively. The structural isomers, tautomers, and hydrogen bonded forms of these derivatives have been studied by IR, mass spectrometry, UV-VIS spectrophotometry, and ^{1}H and ^{13}C NMR, including 2D COSY, 2D J-resolved, and ^{1}H-detected (inverse) single and multiple bond 2D carbon-proton chemical shift correlation techniques.

The derivatives constitute excellent model systems for studying of the various mechanisms involved in the formation of carbohydrate osazones, and are also potential dyes, indicators, and metal-complexing reagents.

11. Thermodynamics of Biochemical Reactions

R.N. Goldberg, Y.B. Tewari, and N. Kishore (Guest Scientist, India)

Equilibrium and calorimetric measurements have been performed on the following reactions:

AMP(aq) + H_2O(liq) = IMP(aq) + ammonia(aq) (1)
adenosine + H_2O(liq) = inosine(aq) + ammonia(aq) (2)
AMP + H_2O(liq) = adenosine(aq) + orthophosphate(aq) (3)
IMP + H_2O(liq) = inosine(aq) + orthophosphate(aq) (4)

Here, AMP and IMP are, respectively, adenosine 5'-monophosphate and inosine 5'-monophosphate. Reactions (1) and (2) are catalyzed, respectively, by adenylic acid deaminase and by adenosine deaminase. Alkaline phosphatase has been used to catalyze reactions (3) and (4). The results of these reactions have been examined in respect to the thermodynamic cycle which they form as well as other thermodynamic data on ammonia elimination and dephosphorylation reactions. Thus, the existence of a substantive body of data on related reactions should serve as a basis for the development of generalizations and estimation schemes for other similar reactions.

Work on the construction of a database on the thermodynamics of enzyme-catalyzed reactions has continued with emphasis on the abstracting of data from the primary literature. The aim is to produce a definitive reference work containing equilibrium and calorimetric data on all enzyme-catalyzed reactions (see "Enzyme Nomenclature - Recommendations of the Nomenclature Committee of the International Union of Biochemistry"). Currently, the data base contains 450 pages of abstracts and approximately 1500 references.

Calorimetric measurements have been performed on the following reactions:

$$\text{L-arginine(aq)} + H_2O(l) = \text{L-ornithine(aq)} + \text{urea(aq)} \qquad (5)$$
$$\text{L-arginine(aq)} + H_2O(l) = \text{L-citrulline(aq)} + \text{ammonia(aq)} \qquad (6)$$

Reactions (5) and (6) are catalyzed by arginase and by arginine deiminase, respectively. Equilibrium measurements were also attempted using high-pressure liquid-chromatography and a fluorescence detector. The position of equilibrium, however, lies very much to the right in both cases, and it was not possible to measure equilibrium constants for these two reactions. The thermodynamic results obtained here can be used, with estimated entropy changes and with other results from the literature, to obtain apparent equilibrium constants for the reactions in the metabolic urea cycle.

As a part of the work of the IUPAC Commission on Thermodynamics, a paper has been prepared which gives information on the conversion of previous temperature scales (the Normal Hydrogen Scale, ITS-27, IPTS-48, IPTS-68, and EPT-76) to the current one (ITS-90). The paper also contains information on the conversion of thermodynamic results obtained on these earlier scales to the ITS-90 scale and the results of sample calculations on a variety of substances over a wide temperature range (16 K to 2800 K). The finding is that only the most accurate results justify a concern about the changes in the temperature scale, and the vast majority of thermodynamic results will be unaffected by these changes within the uncertainties of the measurements.

12. Dynamic Light Scattering of Biomacromolecular Solutions

A.K. Gaigalas and H.H. Weetall

The detection of antigen-antibody reactions using dynamic light scattering from antigen-coated particles has been successfully demonstrated. The antigen which coated the particles was BSA, and the particles were 40 to 60 nanometers in diameter and consisted of a ferrous material. A substantial change in the scattered light autocorrelation function was observed when antibodies to BSA were introduced into the solution of particles. Several characteristics of the autocorrelation function were combined into an indicator whose value depended on antibody concentration. The detection limit for BSA was approximately 50 ng/mL.

In another set of experiments, photon correlations were observed in scattering from silver electrodes. Two distinct time scales were observed in the autocorrelation function; a 1ms and 100 ms. The 1ms decay in the autocorrelation was dominant during voltage cycling while the 100 ms decay was present at all times in varying strength. The slow correlation was associated with microscopic surface height modulation during electrocrystallization, while the fast decay could originate from a dynamic surface polarizability or minute amounts of precipitates. Further work is underway to study correlations in scattering from surfaces.

13. Surface Enhanced Raman Spectroscopy of Biosystems

V. Reipa (Guest Scientist)

The Surface Enhanced Raman Spectrum (SERS) of benzylpenicillin adsorbed on a silver electrode was investigated and vibrational assignments carried out. Comparison with the powder Raman spectrum demonstrated that the benzene ring is in a vertical position relative to the electrode surface. The molecule is bonded to the silver surface through the carboxylate group and the tertiary nitrogen of the beta-lactam ring, resulting in the formation of a bidentate surface complex. Evidence of partial hydrolysis of the benzylpenicillin into 6-aminopenicillanic acid and phenyl acetic acid on the surface of the electrode is presented.

Preliminary measurement of the SERS of bovine insulin, adsorbed from aqueous solutions of ca. 0.01 micromolar concentration, demonstrated the possibility of direct observation of the electrolytic reduction of protein disulfide bonds. Current experiments are aimed at following the enzyme conformational changes associated with this reaction.

14. AC Electric Field Effects on Enzyme Catalysis

R.D. Astumian and B. Robertson

The investigation of the effects of ac electric fields on ion transport and catalysis by enzymes is being continued. Recent results demonstrate that important kinetic parameters can be obtained by making steady-state measurements as a function of the frequency and amplitude of an applied ac electric field. This has been used to determine rapid kinetic parameters for several membrane enzymes: Na^+-K^+-ATPase in erythrocytes, F0F1 ATP-synthase in submitochondrial particles, and a membrane ATPase in plant protoplasts. We are currently working on extending this technique to determine kinetic parameters of soluble enzymes bound to electrodes in order to enhance biotechnologically significant reactions.

Our work also suggests that apparent equilibrium constants can be shifted by an applied ac field if the affinity for substrate is much different than for product. This may be very important for designing electrodes to selectively enhance desired reactions.

15. Mechanisms of DNA Damage

M. Dizdaroglu, Z. Nackerdien (Guest Scientist), and R. Olinski (Guest Scientist)

This project, supported in part by the Department of Energy and the National Institutes of Health, is focussed on the studies of the effects of ionizing radiation and other free radical-producing systems on chromatin DNA *in vitro* and in living mammalian cells. DNA damage in chromatin is studied, with the emphasis on the chemical characterization and quantitation of chemical changes occurring in different constituents of DNA at the molecular level. Analytical methodologies developed in this laboratory can measure ≈1 damaged base (lesion) in 10^6 DNA nucleotides.

Hydrogen peroxide, formed in aerobic cells, has many toxic effects on those cells, including mutagenicity and carcinogenicity. Its toxicity is likely due to its reactions with intracellular metal ions to produce free radicals that can damage biological molecules, including DNA. The formation of DNA-protein cross-links in mammalian chromatin, produced by hydrogen peroxide in the presence of iron ions or copper ions, was investigated. Analysis by GC/MS of chromatin samples exposed to hydrogen peroxide and metal ions revealed the presence of DNA-protein cross-links involving thymine and tyrosine. Other DNA-protein cross-links, which were known to occur in chromatin upon γ-irradiation under anoxic conditions, were not observed. This was due to inhibition by oxygen as shown by results obtained using ionizing radiation under both oxic and anoxic conditions instead of using hydrogen peroxide and metal ions. Substantial differences were observed between the effects of iron ions and copper ions on DNA-protein cross-linking.

The ability of nickel ions or cobalt ions to modify DNA bases in isolated human chromatin was studied. For some time, various nickel and cobalt compounds have been known to be carcinogenic to humans and animals. However, the mechanisms underlying the toxicity of these compounds have remained elusive. In this study, a number of DNA base products were identified and quantitated in samples of isolated human chromatin, which were exposed to nickel ions or cobalt ions in the absence or presence of hydrogen peroxide. Results indicated that mechanisms underlying the DNA damage in chromatin by nickel and cobalt ions may involve hydroxyl radicals.

Another study documented the removal of modified DNA bases from DNA by a DNA glycosylase, namely the Fpg protein, which is a DNA repair enzyme. DNA, which was either γ-irradiated or illuminated by visible light in the presence of methylene blue, was used as a substrate for this study. These two different treatments are known to cause damage to the bases in DNA, although the damage occurs by two different mechanisms. Results showed that the enzyme removed only 8-hydroxypurines and formamidopyrimidines from γ-irradiated DNA and from methylene blue/light-treated DNA. These are the products of hydroxyl radical attack on purines in DNA. Twelve other products resulted from pyrimidines in γ-irradiated DNA were not removed by this enzyme.

16. Statistical Mechanics Studies of Polymer Solutions

J. Hubbard

A remarkably simple and useful identity between the hydrodynamic friction on a macromolecule or Brownian particle of arbitrary shape and the electrostatic capacitance of this object was discovered in collaboration with Dr. J. Douglas of the Polymer Division. Thus, capacitance, which is far easier to calculate than viscous friction, provides an exact measure of solvent-accessible surface area of a macromolecule. In conjunction with accurate measurements of macromolecular diffusion coefficients (via dynamic light scattering or some other technique), this computational and conceptual simplification should prove useful to the study of shapes of solvated macromolecules and in particular biological species.

17. The Three-Dimensional Structure of the 3-3 Isozyme of Glutathione S-transferase from Rat Liver

G. Gilliland, X. Ji (CARB/Univ. MD), and R. Armstrong (Univ. of MD)

The crystal structure of the 3-3 isozyme of glutathione transferase from rat liver has been determined at 2.0 Å resolution. This enzyme plays an important role in the chemical and physical disposition of toxic substances, and is involved in the metabolism of many drugs. The dimeric structure is composed of two identical monomers with molecular weights of 25,000 which have two domains, an α/β and an α domain. The structure has been solved by the multiple isomorphous replacement procedure, which produces an electron density map that has been used to produce the initial model. This model is currently being refined. Knowledge of the final structure of this protein, and its complexes with ligands, substrates, and inhibitors, will be useful in understanding both the reaction mechanism of this enzyme and the substrate specificity. This structural investigation is being done in collaboration with Professor Richard Armstrong of the Department of Chemistry and Biochemistry, University of Maryland, College Park.

18. Interfacing the Biological Macromolecule Crystallization Database to the ICN Micromedics Crystallization Robot

M. Tung and G. Gilliland

The NIST/CARB Biological Macromolecule Crystallization Database (BMCD) has been interfaced to the ICN Micromedicals crystallization robotics software under a cooperative research and development agreement. The BMCD is now accessible to crystallization robotics users through the main menu of the robot operations software. This will provide direct access to the recipes of 1476 crystal forms of 930 biological macromolecules which are currently in the database. In addition to providing this information that can be used to set up crystallization experiments for a particular macromolecule, this software will assist the user in the development of crystallization strategies for new or modified macromolecules.

19. Elucidating the Molecular Mechanism of a Protein Foldase: Defining the System and the Role of Each Reaction Component

K. McKenney

Three significant aspects of DNA replication are under investigation, initiation, regulation, and the role of heat shock proteins. The E. coli plasmid P1 origin of replication has been studied because it provides a number of experimental advantages. During this year we have had a major breakthrough in elucidating the role of two heat shock proteins in P1 replication. It was discovered that dnaK and dnaJ heat shock proteins activate the P1 repA sequence specific DNA binding protein in an ATP dependent reaction in the absence of origin DNA. Purified repA protein exists as a dimer of identical subunits. A 1:1 complex of repA dimer with a dimer of dnaJ protein can be made *in vitro* and isolated *in vivo*. Purified dnaK protein acts on this complex to release monomer "activated" repA protein in a conformation that efficiently recognizes and binds to the nineteen base repA operator sites. Thus, the mechanism of heat shock protein activation is the conversion of native repA dimers to repA monomers. The reaction requires ATP and ATP hydrolysis because α-β and β-γ methylene analogs of ATP do not substitute for ATP and are competitive inhibitors of the reaction. Furthermore, heat shock protein activation can be mimicked with chemical denaturants, with simultaneous conversion of repA dimers to monomers. In addition, active repA monomers can be converted back to inactive repA dimers by concentrating repA monomers. These newly made dimers can then be converted to monomers by heat shock proteins dnaJ and dnaK.

This reaction is important because it provides the first example of a reasonably simple reaction involving dnaK and dnaJ with a straightforward assay, sequence specific DNA binding. Interest in the family of heat shock proteins derives in part because of their great degree of conservation throughout nature and their suggested role as chaperones or foldases involved in protein folding and subunit assembly. For example, the E. coli dnaK protein has 50% amino acid identity and 67% similarity with the human hsp70 protein. The structure of an ATP binding amino domain fragment (the first 330 residues of a 700 amino acid protein) of the bovine homolog of dnaK has recently been reported (Flaherty et al., Nature 346, 623-628, 1990). Because of the high degree of conservation among these proteins, we may be able to use this structure to gain insight into dnaK.

In addition to publishing the molecular definition of the P1 origin, three site directed mutants constructed in the P1 repA protein have been characterized and should provide insight into the regulation of initiation and the interaction with the dnaJ and dnaK heat shock proteins. These mutants were made based on genetic evidence, and *in vitro* experiments suggest that one of these repA mutants may "bypass" the requirement for activation by the two heat shock proteins, dnaK and dnaJ.

This work was done in collaboration with Joel Hoskins at CARB and with Dr. Sue Wickner in the Laboratory of Molecular Biology of the National Cancer Institute, NIH, Bethesda, MD.

20. Analysis of the Regulatory Circuits Involved in the Fine Tuning of Adenylate Cyclase Activity Leading to Controlled Levels of cAMP in Escherichia coli

P. Reddy

Adenylate cyclase synthesizes an important second messenger molecule cAMP which is involved in intricate metabolic pathways. The modulation of the activity of adenylate cyclase that leads to the regulation of the concentration of cAMP in the cell is the major focus of this work. One or more of the protein components of the sugar transport pathway namely Enzyme I, HPr and Enzyme III, modulate adenylate cyclase activity. The state of phosphorylation of Enzyme III is believed to be a major candidate in this regulation. Therefore, work has been focused in this direction by creating site directed mutants of the catalytic histidine to glutamine and glutamate with a view that glutamine should represent the unphosphorylated form of Enzyme III and glutamate should represent the phosphorylated form of the protein. Adenylate cyclase activity was determined in a strain of E. coli that has a chromosomal deletion for the gene for Enzyme III. In this strain, the activity of adenylate cyclase and consequently the concentration of cAMP is low. Upon transformation of this strain with a plasmid carrying the gene for wild-type Enzyme III, high level activity of adenylate cyclase can be restored. Interestingly, the glutamine or glutamate mutants of Enzyme III could not restore the high activity of adenylate cyclase because the catalytic histidine can no longer be phosphorylated and consequently Enzyme III remains in the dephosphorylated state. Although histidine to glutamate mutation did not mimic histidine-phosphate, the data clearly demonstrate that phospho-Enzyme III is the activator of adenylate cyclase and dephospho-Enzyme III is the negative regulator of adenylate cyclase. This aspect of the work is a leap in the understanding of the regulation of adenylate cyclase activity.

21. Thermodynamics of Protein-Ligand Interactions

F.P. Schwarz, A. Surolia (Indian Inst. of Science, Bangalore), S. DeLauder (Howard U.), T. Poulos, M. Mauro, and E. Eisenstein (CARB/U. of Maryland)

The thermodynamics of protein-ligand interactions are of fundamental importance in relating protein structure to function. Titration calorimetry which measures the heat accompanying protein-ligand binding reactions has been employed to determine the thermodynamics of various binding reactions.

Lectins are a class of multivalent proteins that bind sugars with a high degree of specificity and are, thus, ideal model systems on which to study the effect of structure on ligand binding to proteins. The legume lectins also require transition metal ion and Ca^{+2} ligands to convert the lectin from an "unlocked form" to a "locked form" capable of binding carbohydrates. Results from titration calorimetry measurements on the binding of Mn^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}, and Cd^{+2} to the metal-less unlocked form of the legume lectin, concanavalin A, show that the binding reaction is essentially entropically driven by the change from the ordered hydration shells of the aqueous ion to the less ordered configuration of the bound state. The binding affinity increases with the ionic potential of the ion, which indicates that the interaction between the metal ion and the amino-acid residues at the binding site is electrostatic. The binding affinity also increases with pH. This arises from protonation of the histidine amino-acid residue at the binding site which competes efficiently with the metal ion binding reaction at low pH. The large endothermic enthalpy observed for the binding reaction arises from the configurational change of the lectin from the unlocked to the locked form upon metal ion binding. This is in contrast to the exothermic sugar to concanavalin A and to the legume lectin, pea lectin, binding reactions which are essentially enthalpically driven by van der Waals interactions between the sugar OH groups and the amino-acid residues at the binding site. The sugar binding reactions are unaffected by changes in ionic strength and pH, and appear to depend on how well the structure of the carbohydrate fits into the structural motif of the lectin at the binding site. This research was performed in collaboration with A. Surolia of I.I.S. in Bangalore, India.

The thermodynamics of F^- and CN^- binding to the iron of the heme group of cytochrome c peroxidase (CCP) has been investigated in collaboration with T. Poulos and M. Mauro of the University of Maryland and S. DeLauder of Howard University. CCP mutants containing different amino-acid substituents near the iron of the cytochrome group have been prepared in order to determine the effects of these substituents on the binding properties of the iron. The binding enthalpy and free energy change of F^- to CCP exhibit a maximum change at pH 6.0 of -79 and -31 kJ mol^{-1}, respectively. Similarly, the binding enthalpy and free energy change of CN^- are -58 and -33 kJ mol^{-1}, respectively, at this pH. Preliminary results show that reducing hydrogen bond formation between the ligand on the iron and a histidine residue in the heme cavity of CCP, by substitution of an aspartate residue by an asparagine residue adjacent to the histidine residue, reduces the binding affinity for the CN^- ligand.

In collaboration with E. Eisenstein (U. of Maryland), the cooperative binding reaction of isoleucine to threonine deaminase was investigated with titration calorimetry. Threonine deaminase has four binding sites and binding to the first site enhances binding to the other sites, and, thus, cooperative binding is observed. Cooperative binding, which is not fully understood, is highly prevalent in nature. From independent determinations of the binding constants to each of the four sites, an average binding enthalpy of -42.3 kJ mol^{-1} was determined for each of the binding sites.

22. Quantum Mechanically Derived Force-Fields for Molecular Modeling

W.J. Stevens, M. Krauss, and N. Gresh (CNRS, Paris)

A very important problem in structural biochemistry is understanding the role of metal ions in determining the structure, stability, and activity of metallo-proteins. Molecular modelling can play a key role in such understanding by providing a microscopic model of the influence of metal ions on electronic structure, molecular interactions, and reactions. Existing empirical force fields are not well-suited for structural modelling of metallo-proteins primarily because there are insufficient data for empirically adjusting force-field parameters, and also because the large electric fields associated with multivalent metal ions introduce strong polarization effects that are not pair-wise additive. One alternative is to develop force fields based on Quantum Chemistry, which can provide a detailed analysis of molecular interactions with metal ions in terms of electrostatics, polarization, charge-transfer, dispersion, and exchange repulsion.

Gresh and coworkers over the past several years have systematically derived a force field for molecular modelling Sum of Interactions Between Fragments computer Ab initio (SIBFA) based on ab initio analysis of molecular interactions, with as few adjustable parameters as possible. The essential features of this force field are the accurate description of non-bonded electrostatic interactions through the use of distributed multipolar representations of molecular electrostatic potentials, and the introduction of non-bonded polarization interactions through distributed atom or fragment point polarizabilities. The latter terms account for many-body effects through the vector additivity of fragment electric fields and the self-consistent polarization of multiple fragments.

We are using the SIBFA approach to develop force fields for molecular interactions with metal ions. A key question is whether these strong interactions can be adequately represented by the usual, perturbative description of non-bonded interactions. Initial investigations have centered on Zn^{+2} and Na^{+1} ions interacting with carbonyls, carboxylates, imidazoles, and water. We have found that the frozen electrostatic and repulsive parts of the interactions can be described reasonably with the usual first-order approximations, but polarization and charge transfer effects are elusive. Current efforts are aimed at detailed analyses of charge transfer and polarization and the development of appropriate models to represent such effects, including non-additivities.

C. Outputs and Interactions (Biotechnology Division)

1. Publications

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2. Talks

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Abramowitz, S., "Bioprocessing Biotechnology Research Subcommittee," Committee of Life Sciences and Health, FCCSET, August 16, 1991.

Abramowitz, S., "Spectroscopic and Thermodynamic Properties of Gas Phase Species of Interest to Ozone Depletion Models," Hebrew University, Jerusalem, Israel, February 27, 1991.

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Astumian, R.D., "Thermal Noise Limit and the Response of Biological Cells to Weak Electric Fields," Bioelectromagnetics Society Meeting, Salt lake City, Utah, June, 1991.

Astumian, R.D., "Frequency Response of Catalytical Reactions in an Oscillating Field," Department of Chemistry, University of Utah, Salt Lake City, Utah, June, 1991.

Astumian, R.D., "Bioelectric Effects in Medicine," Departments of Biochemistry and Surgery, University of Chicago, Chicago, Illinois, July, 1991.

Astumian, R.D., "Effects of AC Electric Fields of Membrane Enzymes," Departments of Biochemistry and Surgery, University of Chicago, Chicago, Illinois, July, 1991.

Astumian, R.D., "Interaction Energy Conformational Flexibility and Free Energy Transduction," Virginia Commonwealth University, Richmond, Virginia, July 1991.

Astumian, R.D., "Frequency Dependence of Enzyme Catalyzed Reactions," Jerusalem, Israel, August, 1991.

Atha, D.A., "Thermodynamic Analysis of Heparin Binding to Antithrombin," 75th Annual Meeting of the American Society for Biochemistry and Molecular Biology, Atlanta, GA, April 22, 1991.

Basch H., Stevens, W.J., and Krauss, M., "Anion Binding to Polar Molecules (poster)," American Chemical Society, New York, August 25, 1991.

Cole, K.D., "Purification of Low Molecular Soybean Protease Inhibitors Using Aqueous Two-Phase Extraction and Polyethylene Glycol Precipitation," American Institute of Chemical Engineers Annual Meeting, Chicago, IL November 14, 1990.

Cole, K.D., "Separation of the Antinutritional Components of Soybeans: Comparison of Precipitation Techniques to Partitioning in Aqueous Two-Phase Extraction Systems," Colorado Biotechnology Symposium, Boulder, CO, September 24, 1991.

Coxon, B., "NMR Studies of the Squaric Acid Phenylhydrazones," The American University, Chemistry Department, Washington, DC, March, 1991.

Coxon, B., "NMR Studies of Cyclobutanetetraone Phenylhydrazones and Anilides," 6th European Symposium on Carbohydrate Chemistry, Edinburgh, Scotland, September 8-13, 1991.

Dizdaroglu, M.M., "Free Radical-Induced DNA Damage in Mammalian Chromatin in Vitro and in Vivo," City of Hope National Medical Center, Duarte, California, November 19, 1990.

Dizdaroglu, M.M., "Mechanisms of Free Radical Action on Mammalian Chromatin," National Cancer Institute, Frederick, Maryland, January 24, 1991.

Dizdaroglu, M.M., "Mechanisms for Free Radical-Induced DNA-Protein Cross-Linking in Mammalian Chromatin," National Institute of Health, Bethesda, Maryland, March 1, 1991.

Dizdaroglu, M.M., "Measurement of DNA Damage by Gas Chromatography-Mass Spectrometry," Toronto, Canada, July 10, 1991.

Dizdaroglu, M.M., "Is There a Relevance of in Vitro DNA to in Vivo DNA Damage," Toronto, Canada, July 11, 1991.

Dizdaroglu, M.M., "Mechanisms of Oxidative DNA Damage in Chromatin In Vitro and in Vivo," University of Dusseldorf, Germany, July 15, 1991.

Dizdaroglu, M.M., "DNA Damage in Chromatin," Mulheim a.d. Ruhr, Germany, July 17, 1991.

Edwards, J.J., "Protein Modulation in Human Cancer Cells as Determined by 2-D Electrophoresis and Image Processing," Washington Chromatography Group, Gaithersburg, MD, November 1990.

Edwards, J.J., "Protein Modulation in Human Melanoma Induced by Interferon-Gamma and Tumor Necrosis Factor: Two-Dimensional Gel Electrophoresis and Computerized Image Analysis," London, England, July 1991.

Edwards, J.J., "Protein Modulation in Human Melanoma Induced by Interferon-Gamma and Tumor Necrosis Factor," Electrophoresis Society, March 1991.

Garmer, D.R. and Krauss, M., "Cobalt Spectroscopy at the Active Site of Carbonic Anhydrase (poster)," American Chemical Society, New York, August 25, 1991.

Gilliland, G., "Crystallization Databases," American Crystallography Association Workshop on Protein Crystallization, Toledo, OH, July 21, 1991.

Gilliland, G., "Implementation of the Siemens Area Detector Software Release 2.1Å for the Huber Four-Circle," 3rd Annual Siemens Area Detector User Group Meeting, Scripps, La Jolla, CA, May 6, 1991.

Glazier, S.A., "Application of A Artificial Neural Network to Multiion Analysis Employing Ion-Selective Electrode Arrays," 201st ACS National Meeting, Atlanta, GA, April 17, 1991.

Glazier, S.A., "Phosphate Ion-Selective Electrode Development," 201st ACS National Meeting, Atlanta, GA, April 17, 1991.

Goldberg, R.N., "Thermodynamics of Biochemical Processes," NIST, Gaithersburg, Maryland, December, 1990.

Goldberg, R.N., "Conversion of Temperatures and Thermodynamic Properties to the Basis of the International Temperature Scale of 1990," DeKalb, Illinois, July, 1991.

Grabbe, E.S., "Characterization of Adsorbed Protein Layers on Thin Nylon Films with Fluorescence Energy Transfer between Protein and Nylon: A Method for Biosensor Analysis," 4th European Conference on the Spectroscopy of Biological Molecules, York, England, September 2, 1991.

Grabbe, E.S., "Characterization of Nylon Thin Films with Immobilized Protein Layers: Methods for Investigating Adsorbed Protein Conformations," 17th Meeting of the Federation of Analytical Chemistry and Spectroscopic Societies, Cleveland, OH, October 11, 1990.

Hancock, D.K., "The Structure of a New Pyoverdine Type Siderophore from Pseudeomonas Fluorescense 244," The Keystone Symposium on Frontiers of NMR in Molecular Biology, Keystone, CO, April 12, 1991.

Horvath, J.J., "In-Situ Fluorescence Measurements for Process Control in Bioreactors," ACS 201st National Meeting, Atlanta, GA, April 17, 1991.

Hubbard, J.B., "Fluctuation-Dominated Reaction Kinetics," Electron Localization in Disordered Materials, and the Excluded Volume Problem in Polymer Physics, National Institutes of Health, Bethesda, Maryland, March 26, 1991.

Kline, M.A., "Questionable Use of DNA Standards for Sizing PCR Products in Small-Format Gels," Forensic Applications of PCR Technology, Quantico, VA, May 29, 1991.

Krauss, M., "Cs Cluster Binding to a GaAs Surface," East Coat Symposium on Chemistry and Physics of Clusters, Johns Hopkins Univ., Baltimore, MD, January 15, 1991.

Krauss, M., "Is the Vanadate Anion a Transition State Analog of the Phosphorane Transition State of RNase A?," Biophys. Dept., Mt. Sinai Medical Center, New York, April 1, 1991.

Krauss, M. and Basch, H., "Is the Vanadate Anion An Analogue of the Phosphorane Transition State in RNase A? (poster)," American Chemical Society, New York, August 25, 1991.

Krauss, M. and Garmer, D.R., "Active Site Analogues and the Mechanism of Carbonic Anhydrase," Chemical Defense Research Conference, Aberdeen Proving Ground, MD, November 14, 1990.

Krauss, M. and Garmer, D.R., "Active Site Ionicity and the Mechanism of Carbonic Anhydrase (poster)," American Chemical Society, New York, August 25, 1991.

McCurley, M.F., "Fiber Optic Chemical Sensors Based on Polymer Swelling," Polymer Gels Workshop Sponsored by Biomedical Engineering and Instrumentation Program, NCRR/NIH, 1990.

McCurley M.F., "Fiber Optic Chemical Sensors Based on Polymer Swelling," The American Chemical Society National Meeting, 1991.

McKenney, K., "Biotechnology and Protein Engineering," Maryland Society of Professional Engineers, Hagerstown, MD, December 14, 1990.

McKenney, K., "DNA Replication in Procaryotes," George Washington Univ., Dept. of Genetics, Washington, DC, October 16, 1990.

McKenney, K., "Genetic Engineering," Southern Engineering Society, Inc., Hagerstown, MD, May 16, 1991.

McKenney, K., "Molecular Biology of the Stress Response," George Washington University School of Medicine, Dept. of Biochemistry and Molcular Biology, Washington, DC, October 17, 1990.

McKenney, K., "Molecular Mechanism of Heat Shock Protein Function," Center for Advanced Research in Biotechnology, Rockville, MD, March 14, 1991.

McKenney, K., "Protein Engineering," The George Washington University Medical Center, Dept. of Biochemistry and Molecular Biology, February 14, 1991.

McKenney, K., "Role of Heat Shock Proteins in Activating the Replication Initiator Protein of Plasmid P1," Gordon Conference on Biological Regulatory Mechanisms, Holderness, New Hampshire, June 17, 1991.

McKenney, K., "The Regulation of Replication of Mini-P1 Plasmid," Life Technologies, Inc., Gaithersburg, MD, January 10, 1991.

McKenney, K., "Tools of Molecular Engineering," The George Washington University Medical Center, Dept. of Biochemistry and Molecular Biology, February 12, 1991.

Plant, A.L., "Flow Injection Immunoanalysis," GBF, Barunsweig, Germany, June 10, 1991.

Plant, A.L., "Liposome Immunoassays," Millipore Corporation, Bedford, MA, August 6, 1991.

Plant, A.L., "The Difference Between Liposomes and Haptens (poster)," Gordon Conference on Biosensors, Newport, Rhode Island, July 23, 1991.

Powell, L.J., "Overview of the NIST Biotechnology Program," National Research Council, Committee on Bioprocess Engineering, May 22, 1991.

Reddy, P., "Cloning and Overproduction of Lethal Gene Products," CARB/NIST Annual Meeting, Rockville, MD,, May 1991.

Reddy, P., "Fine Tuning of *Escherichia coli* Adenylate Cyclase Activity by the Phosphoenolpyruvate: Sugar Phosphotransferase System," Maryland Biotechnology Institute Annual Meeting, Rockville, MD, April 27, 1991.

Reddy, P., "Mapping Domains in Proteins: Dissection of the Regulatory and Catalytic Domains in *Escherichia coli* Adenylate Cyclase," American Society of Biochemistry and Molecular Biology Meeting, New Orleans, LA, April 25, 1991.

Reddy, P., "Mapping Domains in Proteins Using the pRE Expression Vector and a Family of Oligonucleotides: Dissection of *Escherichia coli* Adenylate Cyclase Gene," Maryland Biotechnology Institute Annual Meeting, Rockville, MD, April 27, 1991.

Reddy, P., "Regulation of *Escherichia coli* Adenylate Cyclase by Sugar Transport Proteins," CARB Journal Club, Rockville, MD, March 21, 1991.

Reeder, D.J., "DNA Fingerprinting: Principles, Applications and Recent Developments," Washington Chromatography Discussion Group, Rockville, MD, September 19, 1991.

Reeder, D.J., "NIST Interlaboratory Result of RFLP Testing and Update on Standard Reference Materials," TWGDAM Meeting, Quantico, VA, July 1, 1991.

Reeder, D.J., "NIST Standards Development for RFLP DNA Profiling," Second Annual International Symposium on Human Identification, Madison, WI, April 11, 1991.

Reeder, D.J., "Quality Assurance Issues in Forensics DNA Analysis," A Roundtable Discussion in Forensic Serology, American Academy of Forensics Sciences, Anaheim, CA, February 22, 1991.

Reeder, D.J., "Questionable Use of DNA Standards for Sizing PCR Products in Small-Format Gels," Forensic Applications of PCR Technology, Quantico, VA, May 29, 1991.

Reeder, D.J., "Update on NIST's Prototype Reference Material for RFLP Analysis," TWGDAM Meeting, Quantico, VA, January 23, 1991.

Reeder, D.J., "Update on NIST Standards Activities," TWGDAM Meeting, Quantico, VA, October 10, 1990.

Richie, K.L., "Standards Program at NIST for DNA Profiling," National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, (NOBCCHE), April 14, 1991.

Robertson, B., "Frequency and Amplitude Dependence of the Effect of a Weak Oscillating Field on Biological Systems," Virginia Commonwealth University, Virginia, July 24, 1991.

Sachs, J.R., "Electromechanical Spectroscopy of Poroelastic Media with Fixed Charge," NIH Workshop on Polymer Gels, December 10, 1990.

Schwarz, F.P., "Biothermodynamics at CARB," Department of Biochemistry, University College of Medical Sciences, New Delhi, India, September 27, 1991.

Schwarz, F.P., "*Hot* Interactions between Sugars and Lectins CARB Internal Seminar," CARB, October 5, 1990.

Schwarz, F.P. and Surolia, A., "Thermodynamic Studies of Lectin-Ligand Interactions The 46th Annual Calorimetry Conference," Northern Illinois University, DeKalb, Illinois, July 29th, 1991.

Schwarz, F.P., "Thermodynamics of Protein-Ligand Binding Interactions," Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi, India on September 25, 1991.

Schwarz, F.P., "Titration Calorimetry and Differential Scanning Calorimetry Studies of Lectin-Ligand Interactions," Department of Biochemistry, University of Delhi, New Delhi, India, September 27, 1991.

Seitz, W.R. and McCurley, M.F., "Fiber Optic Sensors Based on Polymer Swelling," Pittsburgh Conference, 1991.

Tewari, Y.B., "Thermodynamics of Some Reactions Involved in Urea Synthesis," DeKalb, Illinois, July 1991.

Todd, P., "Osmotic Dewatering, A New Crystal Growth Process," Colorado School of Mines, October 8, 1990.

Todd, P., "Microgravity Cell Biophysics," The 48th Annual Pittsburgh Diffraction Conference, Huntsville, Alabama, November 1, 1990.

Todd, P., "Bioprocessing Research: An Essential Step in Biotechnology Commercialization," NIST Boulder Laboratories Staff Colloquium Series, November 8, 1990.

Todd, P., "The Living Biological Cell as a Chemical Factory," AIChE Rocky Mountain Local Section Meeting, December 11, 1990.

Todd, P., "Continuous Electrophoretic Liquid Membrane Extraction," University of Colorado Integrated Training for Biotechnology Leadership, January 15, 1991.

Todd, P., "Gravitational Research and Cell and Separation Science," Universities Space Research Association Workshop on Macromolecular Assemblies and Interfacial Phenomena in Biological Systems, Atlanta, Georgia, April 15, 1991.

Todd, P., "Electrolyte Transport in Charge-Dependent Two-Polymer Systems: Applications of the Low-Gravity Environment," 7th International Conference on Partitioning in Aqueous Two-Phase Systems, New Orleans, June 4, 1991.

Todd, P., "Electrokinetic Demixing of Two-Polymer Systems: Role of Dissolved Phosphate Ions," 7th International Conference on Partitioning in Aqueous Two-Phase Systems, New Orleans, June 7, 1991.

Weetall, H.H., "Biosensors: Fundamentals and Applications," Environmental Protection Agency, Research Triangle Park, NC, May 1991.

Weetall, H.H., "Photochemical Immunoassay," Biosensors Symposium, National Meeting of the American Chemical Society, Atlanta, GA, April 15, 1991.

Wickner, S., Hoskins, J. and McKenney, K., "Role of Heat Shock Proteins dnaJ, dnaK and grpE in the *in vitro* Replication of P1 DNA (poster)," Gordon Conference on Nucleic Acids, New Hampton, NH, June 12, 1991.

3. Patent Awards and Applications

Cole, K.D., Purification of Protease Inhibitors and Protein Extracts Using Polymer Precipitation and Aqueous Two-Phase Extraction Systems Composed of Poly and Salt Solutions (Submitted)

Weetall, H.H., Device and Method for Determination and Detection of Compounds which Intercalate with DNA (Submitted)

4. Committee Assignments

K.D. Cole
Colorado Institute for Research in Biotechnology (Board of Directors)

J.J. Edwards
ASTM E-48 on Biotechnology

D.K. Hancock
U.S. National Committee on Sugar Analysis, Subcommitte 6 on Quartz Control Plates (Referee)
International Commission for Uniform Methods of Sugar Analysis, Subject 5, (Associate Referee)
Washington Editorial Review Board (WERB)

J.J. Horvath
Optical Society of America 1991 Tellers Committee (Chair)

K. McKenney
Ph.D. Examining Committee (Andra Miller), Graduate School of Arts and Sciences, The George Washington University, Washington, DC, February 7, 1991
Ph.D. Examining Committee (June Kaplow), Graduate School of Arts and Sciences, The George Washington University, Washington, DC, February 14, 1991

Advisory Committee for the Dept. of Molecular and Plasmid Biology, American Type Culture Collection, Rockville, MD

L. Powell

American Chemical Society
- Society Committee on Budget and Finance (Vice-Chair)
- Women Chemist Committee (Associate Member)

Chemical Society of Washington (Washington, DC Local Section, ACS): Elected Representative, ACS Council
- Budget Committee (Chair)

Biotechnology Research Subcommittee of FCCSET Committee on Life Science and Health (NIST Representative)

BRS of FCCSETT, Working Group on General/Foundations and Infrastructure

D.J. Reeder

AACC Committee on Standards; Study Group on Total Serum Protein

Electrophoresis Society (President)

IFCC Expert Panel on Durg Effects in Clinical Chemistry (Associate Member)

NIST Animal Care and Use Committee (Chair)

NCCLS Subcommittee on Total Protein

NCCLS Area Committee on Molecular Methods

F. Schwarz

Washington Editorial Review Board (WERB)

IUPAC Exploratory Sub-committee on Data Base of the Thermodynamic Stabilities of Natural and Mutant Proteins which is part of the Steering Committee on Biophysical Chemistry

5. Other

a. Editorships

G.L. Gilliland

Proceedings of the Third International Conference on Crystallization of Biological Macromolecules, Washington, DC, USA 13-19, August 1989. Printed as a complete volume of the Journal of Crystal Growth, Volume 110, (1991), pp. 1-338 (co-editor)

H. Weetall

Applied Biochemical and Biotechnology (executive editor)

b. Seminars

October 8, 1990

Dr. Edward D. Korn, Laboratory of Cell Biology, National Institutes of Health, Bethesda, MD, "The Molecular Basis of Cell Motility." (Division Sponsor: G. Gilliland)

October 22, 1990

Dr. Ralph Pollack, Dept. of Chemistry and Biochemistry, Univ. of Maryland Baltimore County, Baltimore, MD, "Steroid Isomerase: Anatomy of an Enzyme." (Division Sponsor: G. Gilliland)

October 29, 1991

Dr. T.N. Bhat, Institute of Pasteur, Paris, France, "Small Rearrangements in Structures of Fv and Fab Fragments of Antibody D1.3 on Antigen Binding." (Division Sponsor: G. Gilliland)

November 5, 1990

Dr. Julian M. Sturtevant, Dept. of Chemistry, Yale University, New Haven, CT, "Effect of Amino Acid Replacements on the Thermodynamics of Processes Involving Proteins." (Division Sponsor: F. Schwarz)

November 13, 1990

Prof. Alexander S. Spirin, Academy of Sciences of the USSR, "Cell-Free Protein Synthesis Bioreactor." (Division Sponsor: G. Gilliland)

November 19, 1990

Dr. Dorothy Beckett, Dept. of Chemistry and Biochemistry, Univ. of Maryland Baltimore County, Baltimore, MD, "Genetic and Thermodynamic Analysis of Bacteriophage Lambda cI Repressor Cooperativity." (Division Sponsor: G. Gilliland)

November 26, 1990

Dr. Nohad Gresh, Centre National de la Recherche Scientifique, Paris, France, "Base Sequence Preferences in Oligonucleotide Intercalating Drug Complexes. Theroretical Design of Novel, Four to Six Base Pair Sequence Selective Derivatives of Mitoxantrone." (Division Sponsor: W. Stevens)

December 3, 1990

Dr. John Gerlt, Dept. of Chemistry and Biochemistry, Univ. of Maryland College Park, College Park, MD, "Structure-Function Relationships in Mandelate Metabolism." (Division Sponsor: G. Gilliland)

December 7, 1990

Dr. Marc Whitlow, Genex Corporation, Gaithersburg, MD, "Single Chain Antigen Binding Proteins: Recent Results with Anti-Fluorescein and Anti-Tumor Model Systems." (Division Sponsor: G. Gilliland)

December 10, 1990

Dr. Harel Weinstein, Dept. of Physiology and Biophysics, Mount Sinai School of Medicine, New York, NY, "Structural Dynamics of Calcium Binding Proteins: Calmodulin and Troponin-C in Model Solvent Environments." (Division Sponsor: G. Gilliland)

December 17, 1990

Dr. Boaz Shaanan, Laboratory of Molecular Biology, National Institutes of Health, Bethesda, MD, "A Look at Ordered Carbohydrate Chains in Glycoproteins: The Three-Dimensional Structure of *Erythrina coroallodendron* Lectin at 2.0 Å Resolution." (Division Sponsor: G. Gilliland)

January 14, 1991

Dr. Fred E. Cohen, Dept. of Pharmaceutical Chemistry, University of Caifornia, San Francisco, California, "Computational Approaches to the Prediction of Protein Structure." (Division Sponsor: G. Gilliland)

January 25, 1991

Dr. Nikola Pavletich, Dept. of Molecular Biology and Genetics, The Johns Hopkins School of Medicine, Baltimore, MD, "Crystal Structure of a Zinc Finger-DNA Complex at 2.1 Å Resolution: A Framework for Understanding How Zinc Fingers Recognize DNA." (Division Sponsor: G. Gilliland)

January 28, 1991

Dr. Ernesto Freire, Dept. of Biology, The Johns Hopkins Univ., Baltimore, MD, "The Molecular Basis of Cooperativity in Protein Folding." (Division Sponsor: G. Gilliland)

February 4, 1991

Dr. Stephen Sprang, Howard Hughes Medical Institute, Univ. of Texas Health Science Center at Dallas, TX, "Structural Studies of Tumor Necrosis Factor and Fibroblast Growth Factor and What They Tell Us About Receptor Binding." (Division Sponsor: G. Gilliland)

February 11, 1991

Dr. John Collins, Dept. of Biological Chemistry, Univ. of Maryland School of Medicine, Baltimore, MD, "Comparative Structure-Function Studies on Troponin and Myosin." (Division Sponsor: G. Gilliland)

February 15, 1991

Professor John Moult, Center for Advanced Research in Biotechnology, Rockville, MD, "How Do Proteins Fold?" (Division Sponsor: G. Gilliland)

March 7, 1991

Dr. Alexander Makarov, Engelhardt Institute of Molecular Biology of the USSR Academny of Sciences, "Energetic Domains in Globular Proteins." (Division sponsor: R. Goldberg)

March 11, 1991

Dr. Prem Reddy, Wistar Institute of Anatomy and Biology, Univ. of Pennsylvania, "Myb Oncogene: Structure and Function." (Division Sponsor: G. Gilliland)

March 15, 1991

Professor John W. Kozarich, Dept. of Chemistry and Biochemistry, Univ. of Maryland, College Park, MD, "Mechanistic and Structural Aspects of DNA-Drug Interactions." (Division Sponsor: G. Gilliland)

March 25, 1991

Dr. Paula Fitzgerald, Merck, Sharp and Dohme Research Labs, Philadelphia, PA, "The Protease from the Human Immunodeficience Virus: The Role of Asymmetry in a Symmetrical Enzyme." (Division Sponsor: G. Gilliland)

March 27, 1991

Dr. Robert A. Alberty, Chemistry Department, Massachusetts Institute of Technology, "The Fundamental Equation of Thermodynamics for Biochemical Reactions." (Division Sponsor: R. Goldberg)

April 8, 1991

Dr. Ken A. Dill, Dept. of Pharmaceutical Chemistry, Univ. of California, San Francisco, CA, "On the Origins of Structure in Globular Proteins." (Division Sponsor: G. Gilliland)

April 12, 1991

Prof. Ken Showalter, Department of Chemistry, University of West Virginia, "Propagating Chemical Waves." (Division Sponsor: D. Astumian)

April 19, 1991

Dr. Craig Hyde, Laboratory of Molecular Biology, National Institutes of Health, Bethesda, MD, "The Structure of Tryptophan Synthase-a Channeling Multienzyme Complex." (Division Sponsor: G. Gilliland)

April 22, 1991

Dr. Gary Drobny, Dept. of Chemistry, Univ. of Washington, Seattle, WA, "Solid-State NMR Study of DNA Structure and Dynamics." (Division Sponsor: G. Gilliland)

April 25, 1991

Prof. René LeSage, Ph.D., University of Quebec at Trois-Rivieres, "Determination of the Intrinsic Association Constant For the Adsorption of Divalent Cations (Mg^{2+}, Mn^{2+} and Ca^{2+}) on Anionic Phospholipid Membranes." (Division Sponsor: A. Gaigalas)

April 29, 1991

Prof. John Ross, Department of Chemistry, Stanford University, "Thermodynamics Far From Equilibrium." (Division Sponsor: D. Astumian)

May 8, 1991

Dr. Maciej Zylicz, Dept. of Molecular Biology, University of Gdansk, Poland, "Role of Heat Shock Proteins in the Stability of RNA Polymerase and Lambda Replication." (Division Sponsor: K. McKenney)

May 13, 1991

Dr. Patrick J. Fleming, Dept. of Biochemistry and Molecular Biology, Georgetown Univ. Medical Center, Washington, DC, "Structure-Function Studies on the Chromaffin Vessicle Electron Transfer System." (Division Sponsor: G. Gilliland)

May 20, 1991

Dr. Robert Sauer, Dept. of Biology, Massachusetts Inst. of Technology, Boston, MA, "Genetic Dissection of Protein Structure and Stability." (Division Sponsor: G. Gilliland)

June 12, 1991

Dr. Thomas Poulos, Director, Center for Advanced Research in Biotechnology, Rockville, MD, "Structural Aspects of Enzyme Catalyzed Peroxide/O_2 Activation and Interprotein Electron Transfer Reactions." (Division Sponsor: K. McKenney)

August 1, 1991

Dr. T.N. Bhat, Dept. of Immunology, Institute of Pasteur, Paris, France, "Crystallographic Studies of Antigen-Antibody Interactions." (Division Sponsor: G. Gilliland)

August 20, 1991

Prof. D. Schulte-Frohlinde, Max-Planck-Institute, "Defined Damages in DNA and Their Biological Consequences." (Division Sponsor: M. Dizdaroglu)

September 20, 1991

Dr. Johannes Buchner, Institut fur Biophysik und Physikalische Biochemie, Universitat Regensburg, Germany, "GroE Facilitates Refolding of Citrate Synthase." (Division Sponsor: K. McKenney)

September 23, 1991

Dr. Geoffrey J. Howlett, Dept. of Biochemistry, Univ. of Melbourne, Melbourne, Australia, "Analysis of Protein-Protein and Protein-Lipid Interactions by Sedimentation Equilibrium." (Division Sponsor: G. Gilliland)

c. Faculty Appointments

M.M. Dizdaroglu

Adjunct Professor of the Department of Chemical and Biochemical Engineering, University of Maryland Baltimore County

G. Gilliland

Adjunct Professor of the Maryland Biotechnology Institute of the University of Maryland

Adjunct Assistant Professor, Graduate Genetics Program, The George Washington University (1991)

M. Krauss

Adjunct Professor of the Maryland Biotechnology Institute of the University of Maryland

K. McKenney

Adjunct Associate Professor of Biochemistry and Molecular Biology, The George Washington University School of Medicine and Health, Washington, DC

Adjunct Associate Professor of Genetics, The George Washington University Graduate School of Arts and Sciences, Washington, DC

Adjunct Associate Professor of the Maryland Biotechnology Institute of the University of Maryland

P. Reddy

Adjunct Assistant Professor of the Maryland Biotechnology Institute of the University of Maryland

F.P. Schwarz

Adjunct Associate Professor of the Maryland Biotechnology Institute, University of Maryland

W.J. Stevens

Adjunct Professor of the Maryland Biotechnology Institute, University of Maryland

d. Conferences/Workshops Sponsored/Co-Sponsored

May 16-18, 1991

Mid-Atlantic Protein Crystallography Workshop, CARB, Rockville, MD

e. **SRM Activities**

2390 DNA Profiling Standard

f. **SRD Activities**

NIST/CARB Biomacromolecular Crystallization Database, Update

CHEMICAL ENGINEERING

II. Chemical Engineering Division (832)

Blaine Bateman, Chief

A. Division Overview

Dramatic changes impacted the Chemical Engineering division in fiscal year 1991. The division lost five permanent staff by a reduction in force (RIF), two senior staff retired from the fluid metrology area (including the Group Leader of System Dynamics), and five employees were transferred to the Biotechnology Division in Gaithersburg. In May, a new Division Chief was named, and in October the transfer to the Materials Science and Engineering Laboratory of seven staff in solids research was announced, including the Group Leader of Properties of Solids. Thus, we have lost 19 staff, including two managers, and had a change in Division Chief.

Division finances were an issue the entire year, precipitating the RIF and, combined with the other organizational changes, leading to an unsettled atmosphere most of the second half of the year. The traditional reliance on other agency funds for as much as 80 percent of our research was upset by a difficult funding situation in the first half of the year. While the staff performed extremely well to meet new other agency commitments late in the year, the concern over short-term funds versus long-term programs, and the difficulty in focusing so many other agency efforts towards our division goals, remained. Many of the staff losses were accompanied by funding reductions, so that the overall funding outlook is still difficult for FY92.

Aside from the financial upsets, the personnel losses have disrupted ongoing and planned efforts. However, we now have a staff profile more closely aligned with potential goals of a chemical engineering program. Opportunity and challenge exist to focus our work and contribute to the solution of national problems and to technological advances. In FY92 we will redefine and sharpen our focus; emphasis will include technology and data aimed at the chemical process industries and the solution of environmental issues. We plan a major thrust in computational engineering to enhance the value of our traditional laboratory measurement programs.

In FY91 the Chemical Engineering Division included basic and applied research programs in separation technology, reactor engineering, heat and mass transfer, advanced materials, and fluid dynamics. Modelling and simulation were coupled with experimental research to increase the availability of results; our customers accessed not only experimental data and analysis, but predictive models and correlations as well. Division scientists developed essential engineering measurement methods and data bases to support the design of advanced chemical processes. The products of the division are important to the competitiveness of many U.S. industries including oil and gas, chemicals, minerals and mining, aerospace, electronics, power generation, and others. Programs were maintained in the Transport Processes, System Dynamics, and Properties of Solids groups. About half-way through the year, activities in System Dynamics were consolidated into the other two groups upon retirement of the System Dynamics Group Leader.

Transport processes research focuses on separations, heat transfer, mass transfer, and chemical reactor dynamics. Reversible chemical complexation, interactions in ion-exchange media, and other highly selective methods are explored to separate and purify gases and liquids, with applications including removing acid gases from natural gas, and separation of protein products from biotechnology processes. Heat and mass transfer are studied in novel systems, such as supercritical fluid extraction, providing data and models to develop more efficient processes for industry. Chemical engineering solutions to chemical process problems are studied in the framework of novel reactor systems, including reactor design for environmental applications.

Research in Properties of Solids includes determining the thermal and chemical behavior of materials--from insulations to advanced composites, and research in fluid dynamics. Programs are underway to develop flowmeters for the Space Shuttle, and to determine the effects of disturbances on flow measurement. Unique expertise is developed and maintained for the measurement and standardization of thermal conductivity of materials at low temperatures. Other areas of research include cryogenic refrigeration using pulse-tube technology, adsorption on high surface area solids, tribology, and rapid oxidation.

A brief summary of some of the research thrusts is provided here; greater detail will be found in the specific technical descriptions.

Membrane Separations

Despite the rapid growth of this energy efficient technology, much still needs to be done to facilitate a rational approach to design. This program is designed to address this deficiency by improving the understanding of mechanisms of molecular transport. In gas separations, using ion-exchange polymer resins, efforts are directed toward the study of how membrane morphology and chemistry affect transport of molecular species. Changes in morphology are effected by ion replacement, heat treatment, and by the introduction of dopants in the casting stage of preparation. (A patent application has been made in the latter case with collaborators at the University of Colorado Center for Separations Using Thin Films). Small Angle X-ray Scattering (SAXS) measurements carried out in collaboration with colleagues of the Polymers Division are used in probing changes in morphology. Finally, changes in morphology are correlated with changes in the observed membrane performance.

Ultrafiltration is a technology which finds applications in separating or concentrating macromolecules such as those found in paint processing, food processing, polymer preparation and protein purification. The most critical issue affecting commercialization is the prevention of membrane fouling since retained molecules tend to build up a surface adsorbed layer on the membrane resulting in irreversible flux decline. Experimental methods have been developed for characterizing flux decline, and a study is underway investigating membrane surface modification through chemical bonding to prevent irreversible adsorption.

A guest researcher from the University of Bombay was sponsored by the US-India fund to study pervaporation, a promising method of breaking azeotropes and removing undesirable light components from chemical and biochemical reactors. This extended the work of earlier collaborations in which a model of the process had been developed and tested.

Large-Scale Adsorption and Chromatography

In many processes in the food and beverage industries, and in pharmaceutical manufacture, a large-scale chromatographic separation is often the preferred final stage of intermediate or product purification. This relatively new application of chromatography relies a good deal on empiricism and rules of thumb. Therefore an opportunity exists to help provide a rational basis for design of efficient systems. Areas of study may include the correlation of partitioning data, physico-chemical evaluation of media, column hydrodynamics, and process control to improve column utilization and product purity.

A new column medium was evaluated under a Cooperative Research and Development Agreement (CRDA) with an industrial collaborator, and an economic appraisal of media particle size was conducted based on a theoretical transport model. The use of Low Angle Neutron Scattering was investigated as a tool for correlating the degree of crosslinking in a size exclusion medium with thermodynamic data, and a thermodynamic model was developed.

In a related area, a Department of Energy-sponsored study of convection and dispersion in packed beds with density gradients continued the development of a novel facility for bed hydrodynamics studies. The system we have developed is based on the use of fiberoptic laser fluorescence probes used in conjunction with fluorescent dye tracers, and permits the measurement of convective flow cells caused by thermal gradients and packing inhomogeneities.

Supercritical Fluid Extraction

The use of compressed gases as solvents, either as liquids or supercritical fluids, offers flexibility in processing and the unique advantage of almost complete separation of solvent from product at moderate temperatures. This is of particular interest in food processing where new products such as cholesterol-free dairy products may be manufactured and where toxicological hazards must be eliminated. In hydrocarbon processing, the economics are favored because compressed gas solvents are often already present. Problems addressed revolve around the need to be able to characterize extraction processes and model extraction rates from raw materials. Earlier work dealt with the need to model heat and mass transfer in the further handling of the solute-laden solvent, such as in solvent recovery by retrograde condensation. Progress was made toward the completion of a computational model.

As part of the development of a technique to measure extraction rates, the problem of real-time process monitoring was solved by the design, construction, and testing of a high-pressure near-infrared transmission cell remotely coupled to a Fourier Transform-Infrared (FT-IR) spectrometer by fiberoptics. Quantitation was verified for several organics in supercritical carbon dioxide.

Chemical Reaction Engineering

The study of heat and mass transport along with chemical kinetics are key to the design and theoretical description of commercial scale chemical reactors. In this new program area, problems of disposal of military ordnance are being studied. In another project, production of molecular oxygen in electronically excited states is studied as the active medium in a chemical laser. The merits of alternative reactor configurations are evaluated. Opportunities exist to employ chemical conversions to render hazardous environmental contaminants harmless using novel reactor concepts. This is an area of major national importance and is identified by the administration as a key technology for the 90s.

Thermal Conductivity Measurements

A large area of research deals with the thermal conductivity of advanced composites, ceramics, metals, foams, polymers, fibrous insulations, and multilayer insulations in the temperature range of 4 K to 1500 K. The capability to study transport of thermal energy of such a wide range of materials over the large temperature range is unique. During FY91 two new systems were completed and are being evaluated for precision and bias. Apparatus now in operation include: three guarded-hot-plates (ASTM C-177) covering the temperature range from 4 to 800 K for poor conductors; one boiloff calorimeter which has been modified to allow extremely large temperature differences, 27 to 1100 K, to be imposed on very good insulations; one single sided guarded-hot-plate for studying ceramics and ceramic composites in the temperature range from 400 to 1500 K; and one axial heat flow system for studying rigid materials in the temperature range from 4 to 350 K. A large number of metals, polymer composites, and insulation systems have been studied during FY91. These data and analytical representations have significantly expanded our growing data base for engineering materials. Research results from this area are widely disseminated to both the private sector and other government agencies as well as being part of standards activities in the ISO and ASTM.

Metals Oxidation/Tribology

The effect of harsh environmental conditions such as high and low temperatures, oxidizing atmospheres, and rubbing surfaces is being investigated using dynamic rubbing friction and controlled joule heating to provide the oxidation energy. Friction between rubbing metal surfaces at various loads, velocities, and temperatures in the presence of oxygen is being studied. The stainless alloy 440C is of particular interest to allow a better understanding of the wear mechanisms that can lead to premature failure of turbopump bearings on the Space Shuttle engines. Extensive analysis of the oxides are necessary to interpret the dynamic reactions involved. During FY91 the study was expanded to include diamond-like-carbon films. Preliminary results suggest that the coefficient of friction is reduced nearly an order of magnitude and concomitant wear is slight. A major apparatus is nearing completion which will allow use of differential thermal analysis and thermal gravimetric analysis (DTA/TGA) to study basic oxidation reactions of various metals in a high pressure and high temperature oxygen atmosphere.

Thermodynamics/Heat Transfer

The transfer of heat between the surface of heat exchangers and a high-pressure flowing gas, while very high heat fluxes impinge on the surface, are being studied to better understand basic heat transfer mechanisms that can occur in advanced commercial and military flight vehicles. The design of the heat-transfer surfaces, the fluid conditions, and the high heat fluxes in these applications are not well characterized by classical heat-transfer theory. Experimental results are being compared with existing theory to provide maximum information for design applications.

Heat transfer in regenerative heat exchangers and refrigeration cycles continues to be studied to improve the performance of cryocoolers. In FY90 a patent was granted on the thermoacoustically driven orifice pulse tube refrigerator (TADOPTR); during FY91 increased efficiency was demonstrated to the extent that it is comparable to the Stirling cycle refrigerators in some conditions. This has served to expand potential applications from satellites to private sector use in liquefaction of natural gas at remote sites, and in high-temperature superconductor device cooling. Programs to develop the concept for these and other applications are anticipated for FY92.

Fluid Metrology

The national reference facility for liquid nitrogen flow measurement continues to operate. At the present time this facility has a flow range of 0.02 to 0.23 kg/s. Requests from industrial firms for lower flow rate capabilities have resulted in preliminary designs for modifying the facility. Flow rates down to less than 0.001 kg/s are needed. In collaboration with the Office of Weights and Measures and the Thermophysics Division, national and international standards are being maintained. These standards specify both measurement methodology and thermodynamic properties for use in low temperature liquid flow measurement.

Instrumentation required for fluid handling on the space shuttle and in space applications continues to be an important area of research. Providing test facilities and expertise for evaluating commercially developed instruments has proven to be valuable to both NASA and to the manufacturers. Requirements by NASA for high speed testing of commercial instruments for detecting liquid-vapor interfaces required the construction of a new facility in FY90. Testing new instrumentation in this facility has been very successful. Feasibility of using commercially available devices in low-temperature applications is being studied and the new facility provides a quick and accurate method of testing prototype devices.

Gas-flow measurement continued to be an important area of interest. Revisions to both the U.S. and the international standards dealing with orifice-flow measurement continue. Additional experimental work will be required before existing standards can be brought into agreement. The discrepancies between U.S. and the international standards are increasingly troublesome and will continue to be addressed.

B. Selected Technical Reports (Chemical Engineering Division)

1. Gas and Vapor Separations Using Membranes

J.J. Pellegrino, P.J. Giarratano, R. Rabago (Guest Scientist), T.J. Cirbo, B.W. Wilson, and V.L. Comly (Guest Scientist)

Membrane separation is the use of an interfacial, nonpartitioning phase (usually very thin) to provide a selective barrier between two process phases. In gas separations, mixtures of permeant gases are being separated or purified by the imposition of a partial pressure gradient across the membrane. In vapor separations, condensable components in a gas stream or a liquid mixture are evaporated through the membrane. For vapor separations, either a pressure or temperature gradient is used to provide the mass transfer driving force. Separations using membrane processes can provide advantages either as replacements for or adjuncts to existing separation unit operations. In general, membrane processes potentially can perform a separation at lower energy, capital and operating costs with a greater degree of operational flexibility, simplicity and reliability than other processes. Currently, membranes are being introduced into O_2/N_2 separation, H_2 recovery, natural gas purification, dehydration of alcohols and other organic solvents and removal of organic contaminants from air and water streams.

Our research has focussed on studying chemically specific separations, primarily using immobilized liquid membranes based on the ion-exchange polymer polyperfluorosulfonic acid (PFSA). We have also studied immobilized films of waxes and oils for removal of trace organics (eg., benzene, carbon tetrachloride, 1,1,1-trichlorethane) from water and separation amongst themselves. Our programs have included applications testing, process system analysis and design, transport process modeling and polymer microstructure science.

In a program supported by DoE, Morgantown Energy Technology Center, laboratory and field tests are being performed to ascertain long-term chemical, mechanical and functional stability of PFSA membrane forms in the separation of CO_2 and H_2S from natural gas streams. Selectivity of H_2S vs. CH_4 has been demonstrated to reach as high as 60 but solvent stability in the membrane is still an issue. Future work is focussed on defining solvents with better stability and membrane forms with higher productivity.

In a study of volatile organics separation, a homologous series of paraffinic alcohols (waxes) were immobilized in microporous polypropylene films. The permeation rates of benzene, carbon tetrachloride, 1,1,1-trichlorethane and water were measured. Initial results indicate that this approach could provide a low-cost means to separate the volatile organics, not only from water, but from each other, and this procedure could be used in waste minimization efforts.

In collaboration with the University of Colorado Center for Separations using Thin Films, we have been studying the effect of microstructure modifications of PFSA. Ionic surfactants were incorporated in the casting solutions for PFSA films. These films showed significant microstructure variations in observations of Small Angle X-ray Scattering (SAXS) and permeation behavior for both gases and vapors was influenced. A joint patent application for this work is being filed. Our future work will be to elaborate the relationship between the microstructure and the transport behavior.

A system design study, supported by DoD, was undertaken for water recovery from diesel exhaust. A process evaluation was made of water dehydration membranes and system design. This included the development of an improved membrane modeling algorithm. We plan to develop a module design package which better incorporates internal boundary layers and pressure loss.

2. Coated Thin Film Composite Membranes

J.J. Pellegrino, M.K. Ko, A.P. Peskin, and P.J. Giarratano

In order for a membrane process to be useful, the module must provide an economic level of productivity. This usually requires a thin separating layer for two reasons: 1) diffusion through a thin film provides a higher flux (or productivity) and 2) thinner films can usually pack a greater surface area per unit volume. The desire to form a mechanically strong membrane that has a thin separating layer has usually led to asymmetric membrane casting techniques. This approach has two possible deficiencies: 1) it limits the type of polymer applicable and 2) defects arise which can undermine the diffusive separation process. Therefore we have begun studying the formation of composite membranes. These consist of a thin coating of a specific polymer on top of a mechanically strong and inert microporous (pores greater than 0.02 micrometer diameter) support film.

We are pursuing an "enabling" technology to expand the range of polymers useful for all membrane separations. Our programs include elements of modeling, empirical evaluations and applications testing. We have focussed on casting thin films from polyperfluorosulfonic acid (PFSA) ionomer on a variety of microporous flat sheet supports. We have also started developing an approach for coating the inside of microporous hollow fiber bundles. The key practical question is how thin a film can be made to bridge the pore without filling it up. Also, the casting process significantly influences the polymer's microstructure independent of whether we are forming a composite film or not. This realization has made further evaluation work more problematical.

In the past year, we have coated microporous polypropylene films with PFSA in collaboration with 3M Corporation - partially funded by DoE. Films have been cast at room temperature with varying solids content, various solvents and initial conditions of the state of the porous support. These films are examined using Scanning Electron Microscopy (SEM) and gas permeation studies to determine the physical integrity and characteristics of the film.

Composite thin films have been evaluated in the field test program for separating acid gases from natural gas at Chevron's natural gas plant (supported by DoE-METC). These membranes have good mechanical and chemical integrity, but it is difficult to identify cause and effect for their permeation performance. Since many parameters are being simultaneously changed in the field test environment, we have begun removing membranes from the field and doing further studies on them in a well-controlled laboratory environment.

Finally, we have initiated a modeling effort in collaboration with S. Selim at the Colorado School of Mines and R. Sani at the University of Colorado. An analytical model has been developed for 1-dimensional, multicomponent, isothermal evaporation on a solid surface. A finite element computer code is being adapted to model the 2-D nonisothermal problem including the pore geometry.

3. Membrane Fouling in Ultrafiltration Membranes

M.K. Ko, J.J. Pellegrino, and A.P. Peskin

In ultrafiltration (UF), macromolecules are separated by size under a pressure gradient applied across the membrane. Advantages over conventional separation methods are: (1) there is no phase change during operation, (2) separation occurs at ambient temperature, and (3) a desired selectivity can be relatively easily achieved. Current industrial applications include waste water treatment; recovery, concentration and/or fractionation of valuable products (e.g., organic solvents, inorganic and macromolecules); and in downstream bioprocess separations. In recent years, membranes have also been incorporated into primary unit operations to carry out reaction and separation, simultaneously. In all applications, the pivotal problem limiting commercialization has been fouling of ultrafiltration membranes by irreversible macromolecule adsorption on the membrane surface. This drastically reduces performance (flux and selectivity). It is also a limiting factor for some other membrane processes (reverse osmosis, nanofiltration, microfiltration, and dialysis).

Our research has focused on studying membrane fouling from both interfacial phenomena and engineering viewpoints. Using UF as a model case, we have been working on macromolecule (protein) adsorption on membrane surfaces to study fundamental aspects of membrane fouling mechanisms, transport mechanisms of solutes and solvent near the interface, and properties and structure of the macromolecule-adsorbed layer. We have developed new and unique experimental schemes to characterize membrane materials and their performance, and explained some of the fundamental aspects mentioned. Our goals are aimed at improving the scientific understanding of the fouling process, developing low-fouling membranes, and providing membrane standards in membrane materials and operations.

In the last year, we have been investigating the correlation between interfacial interactions and membrane fouling. Electrostatic potential and dispersion interaction energy among solid surface, solute and aqueous medium are being studied along with filtration behavior in the corresponding environments.

In collaboration with the University of Colorado Chemistry Department, we also investigated the development of a low-fouling membrane by surface modification. A covalently attached "spacer arm", consisting of several linear monosaccahrides connected by peptide bonds, creates a water-buffered layer at the solid surface. It is expected to enhance hydration or lower the binding strength and provide stearic hindrance repulsion to lower the macromolecule binding.

4. Large-Scale Chromatographic Separations

S.R. Rudge (Guest Scientist) and A.P. Peskin

Large-scale chromatography offers solutions to some delicate or difficult industrial separations. Commercial examples include the separations of xylene isomers, sugars, pharmaceuticals and biological molecules. Even though many industrial scale units are marketed and are today in operation, optimum configurations and chromatographic media may be application specific and are probably not known at this time. Depending on application, processing costs may be dominated by the cost of media or labor when frequent replacement of the medium is necessary. This provides strong motivation for research in the characterization of low-cost media, innovative process control strategies, and novel continuous flow configurations.

The division recently initiated a program of research in this area. Work completed this year included an economic analysis of size-exclusion chromatography, where particle size was the parameter of interest, a physico-chemical evaluation of a medium for an industrial collaborator, and the development of a statistical mechanical model of partitioning. The economic analysis was based on a detailed transport model and was carried out for specified resolution. It showed that optimum particle size may be larger than conventional wisdom would allow. This could be attributed to the high cost of small particles. Alternatively, one may conclude that an incentive exists for the development of inexpensive media with small particle size. The statistical mechanical model explored the possibility of correlating partitioning with resin cross-linking for solvent-swollen size-exclusion chromatography. Chain-length parameters were obtained from measurements of screening length of D_2O-swollen size-exclusion gels for various degrees of crosslinking by Low Angle Neutron Scattering (LANS).

Future work will be aimed at identifying and characterizing media and configurations most appropriate to the requirements of large scale separations.

5. Packed Bed Hydrodynamic Studies

J.D. Wolfe, R.D. Nassimbene, and M.C. Jones

The separation efficiency of packings in separation equipment such as adsorption and chromatography columns is to some extent limited by hydrodynamic factors. While a good deal of uniformity can be achieved by particle size control and careful packing procedures, there remain hydrodynamic effects due to channeling and flow maldistribution. The wall effect is well known, but is unimportant provided the bed dimensions are orders-of- magnitude greater than those of the particles. Density and viscosity gradients, however, may still give rise to excess dispersion.

In a Department of Energy funded study of convection and dispersion in packed beds, a new approach to the study of bed hydrodynamics has been developed. Arrays of cleaved optical fibers are installed on a bed boundary - usually the base plane - to detect the presence of a fluorescent dye tracer injected into a throughflow stream and stimulated by laser light from the same fibers. Under isothermal conditions, instantaneous spatial patterns of dye concentration mapped by the array are capable of indicating flow maldistribution or faulted packing. When density or viscosity gradients exist, induced by either concentration or temperature gradients, patterns of nonuniformity of flow, either buoyancy or viscosity driven, can be imaged in the same way. Residence time distributions and transit time statistics can also be used to monitor the state of convection. This innovation in the study of porous media hydrodynamics leads to information not easily available from traditional experimentation. For example, it has been used in a study of the onset of cellular convection in packed beds subject to adverse density gradients. A parallel two-dimensional finite difference computation facilitated the interpretation of the experimental results. The results show that nonuniform flow precursors can be detected with accompanying increase in the dispersion well below the expected transition to cellular flow. It was also found that patterns of cellular convection were strongly dependent on small irregularities in the porosity distribution, contrary to original expectations. These results are important in packed bed separation processes where control of hydrodynamics is considered crucial.

Future plans are to apply this technique to diagnosis of flow dispersion and channeling in packings of commercial interest for large-scale adsorption and chromatography.

6. Supercritical Extraction Dynamics

M.A. Wood, R.M. Stewart, and M.C. Jones

Successful adoption of supercritical fluid extraction in food, fuel and pharmaceutical industries as an industrial processing technique requires a knowledge of extraction mechanisms and data on appropriate processing parameters. These include thermodynamic, kinetic, and transport parameters. In contrast to the laboratory-scale, extraction times for the industrial scale will most likely be determined by mass-transfer rates from the host porous matrix. They may also be kinetically limited where chemical bonding is involved. Our research concentrates on determining rate parameters of mathematical models of extraction. This is done by performing experiments in which these role parameters are inferred from the dynamics of extraction of solutes from single-particle and fixed bed experiments. Alternate configurations to maximize transport rate, such as the use of fluidized beds or slurries, are also of interest, and an overriding concern is the establishment of the solvent thermodynamic states which will optimize the rate.

Apparatus has been developed in which the external mass transfer resistance of ensembles of similar porous particles can be controlled or eliminated in order to measure both internal and external contributions. This has been done by an adaptation of the zero gradient reactor successfully used in catalyst particle kinetics studies in which intense agitation may be provided to the reactor fluid. Transient extraction rate is to be measured by solute uptake, which will be observed by on-line Fourier Transform-Infrared (FT-IR) spectroscopy. A fiberoptic-coupled, high-pressure transmission cell was developed for this purpose and successfully tested using various solutes dissolved in supercritical and compressed liquid CO_2. While some advantage may be gained by further improving the optical matching of fiber with instrument, it was demonstrated that, with this arrangement, sufficient concentration precision can already be achieved for absorption bands not in the vicinity of strong CO_2 vibrational bands in the wavelength range 1 to 4 micrometers. Implementation of the monitor in the dynamic extraction experiments is in progress.

In addition to the experimental investigation, analytical models have been derived for the estimation of extraction times and solution techniques using symbolic mathematical software have been developed.

Future topics of interest include the use of solvent modifiers such as small polar molecules and surfactants to enhance rates of extraction for difficult-to-dissolve polar or ionic solutes, and a study of the advantages which may be obtained from fluidized versus fixed bed operation.

7. Mathematical Modeling of Transport Processes

G.R. Hardin, A.P. Peskin, and J.D. Wolfe

Mathematical modeling and computer solution by numerical means is an indispensable component of our program of research in separation processes. The existence of rigorously founded codes describing such processes permits efficient and relatively inexpensive exploration of system parameters and the detailed observation of behavior helpful to the interpretation of experimental findings. Over the past three years, we have developed a competence focussed in a few selected problem areas. Our staff have experience in finite element and finite difference computations of fluid-based systems involving multicomponent liquid films with phase change, multidimensional flows in porous media, and moving boundary problems. Work has been undertaken in support of experimental investigations in membrane processes, retrograde condensation of supercritical mixtures and packed bed hydrodynamics.

In order to improve understanding of the mechanism by which defects are formed in casting thin composite membrane films, a finite element method is being implemented to study the instabilities of an evaporating liquid film of the order of 100 nm thickness on a nonwetted substrate. Sliding splines are used to track the movement of the interface. Results of this nonlinear computation have verified the role of the most highly amplified wave determined by linear theory, showing such a disturbance to grow rapidly to the point where rupture of the film is imminent. In contrast, disturbances predicted to be stable are damped. Future computations will consider non-Newtonian rheology and the effect of evaporative mass transfer.

In an earlier study, condensation-evaporation transfer from thick binary liquid films with free interfaces was analyzed by linear stability theory in an attempt to understand the role of interfacial-tension-driven flows on combined heat and mass-transfer rates. Some useful results were generated that showed a destabilization at high condensation rates due to convective distortion of the temperature gradient at the interface. A number of prototypical systems are being studied including one for a supercritical fluid (SCF) mixture undergoing retrograde condensation, a process by which solvent can be recovered in SCF extractions.

Finite difference solution of a two-phase, ensemble-averaged form of the Navier-Stokes equations has been implemented to interpret experimental results on convection and dispersion in packed beds. Empirical formulations of the non-Darcy viscous and inertial terms (Brinkman and Forscheimer terms) were incorporated for greater generality, and a novel handling of the stochastic nature of the packing was implemented. This Monte-Carlo-like method assigned a distribution of porosity throughout the bed, having an experimentally based mean and standard deviation. This turns out to be a key property of the code for description of observed dispersion-related and non-steady phenomena. A 3-D version of this code has been developed in collaboration with the Los Alamos National Laboratory, and although initially prohibitively expensive to run, considerable progress has been made recently through vectorization and implementation of an improved sparse-matrix solution scheme.

Future activity in computational chemical engineering is expected to accelerate. We do not expect to be wanting for problems to tackle and we are developing a new object-oriented approach which promises to streamline code development.

8. Chemical Reactor Engineering

J.F. Welch and J.A. Hurley

Chemical reactors are the very heart, and at the same time the Achilles' heel, of the chemical process industry; they are the irreplaceable components of processes in which feedstocks are converted to desirable products, and they are simultaneously the source of almost all of the undesirable organic species present in the environment today. Conversion by chemical reaction to innocuous, benign, or beneficial species is a long-term solution to the management of undesirable species. This program was developed in response to the need to convert extremely toxic (chemical warfare agents) and energetic (propellants and explosives) species in waste streams from Department of Defense industrial activities to innocuous species. Its objectives include the transformation of some of the art of chemical reactor engineering to a scientific basis, development and application of some of the latest computing methods to the modeling of transients in fixed-bed chemical reactors, and demonstration of proof-of-concepts of reaction schemes for conversion of toxic and energetic species to innocuous species.

The products of the program consist of data, models, and proof-of-concepts for novel chemical reactors and reaction schemes; they are derived from a mix of experimental and computational studies of both a fundamental and applied nature. In the past year, these studies have resulted in the development of an atomizing nozzle for injection of a chemical-warfare agent into a high-temperature incinerator; the development and testing of a high-pressure, high-temperature tubular reactor for destruction of a nitrated-glycol; use of a continuous-stirred-tank-reactor for conversion of a hazardous, inorganic military propellant to innocuous compounds; and the development and testing of a fixed-bed oxygen generator.

Computational efforts have been conducted in support of the experimental work and may be classified as process modeling (material and energy balances) for use in environmental impact statements; design; tradeoff analyses; and equipment sizing and specification. In addition, for use in reduction of experimental results and estimation of performance of yet-to-be-built chemical reactors, numerical solutions are found for sets of partial-differential equations (equations of change) which describe chemical reaction and transport processes.

A numerical model developed for homogeneous and heterogenous reactions for laminar flow in a cylindrical tube was useful in the analysis of experiments related to the deactivation of excited oxygen. A spline-smoothing program was coupled with the cross-validation-mean-square-error technique to analyze rate data from experiments; this method can be used for model-free estimation of first and second derivatives from rate data.

Close ties with industry are maintained through Department of Defense sponsored government-industry meetings and programs, and active participation in working groups of the American Society of Testing and Materials (ASTM), American Institute of Chemical Engineers (AIChE), and the Society of Photo-Optical Instrumentation Engineers (SPIE). Collaboration with universities on modeling and specialized chemical analyses provides an additional mechanism for dissemination of program work product.

Closer and more direct cooperation with industry figure strongly in the future efforts in this program. Methods developed for management of extremely toxic and energetic species can be readily adapted for management of hazardous species in wastewater streams associated with the chemical process industry. The results of a recently completed study of the metal-catalyzed decomposition of alkaline hydrogen peroxide into reactive intermediates will be applied to promote the rates of oxidation of hydrocarbons in aqueous solution (wastewater).

9. Thermal Conductivity of Solids

W.P. Dubé, B.J. Filla, D.L. Rule, D.R. Smith, K.A. Cutter, and J. Morgan

A major area of research within the Properties of Solids Group involves the study of the thermal conductivity of materials and systems of materials. The apparatus involved in the study allow an extremely wide range of temperatures to be accessed and materials spanning several orders of magnitude in conductivity to be tested. Apparatus which are operational or in calibration stages include (1) three guarded-hot-plate (GHP) systems for studying thermal insulators, (2) one boiloff calorimeter (HGBOC) which has been modified to allow extremely large temperature gradients to be imposed on the test specimen, (3) a single-sided, very-high-temperature GHP (VHTGHP) specifically designed to study ceramics and ceramic composites, and (4) an unguarded, fixed-point, axial-heat-flow apparatus (FPAXIAL) used to study rigid materials at cryogenic temperatures. All of these systems provide steady-state data, as opposed to transient data. These apparatuses and the expertise of the research team constitute a unique capability in this area.

In FY91 we used FPAXIAL to measure conductivity from 4 to 300 K for SRM 735 stainless steel, SRM 8422 tungsten, BeCu, Al 6061, CuNb, AlLi, for numerous plastic composites, boron nitride, sapphire, and saran carbon. Studies of Be-Cu alloy C17510 showed that the conductivity is very sensitive to the chemical composition. Measurements on 6061 showed that the conductivity is sensitive to the heat treatment of the material. Studies of the Al-Li alloy 2095 showed that its conductivity, mechanical properties and thermal expansion make this alloy a possible cost-saving substitute for the aluminum alloy 2219. Using results from FPAXIAL, a significant data base is being formed for materials being used in advanced designs. The long-term goal is to develop predictive relationships for conductivity based on material properties and conditions.

The VHTGHP became operational this year and has been calibrated to 600 °C. Emphasis is on advanced ceramics and composites, which are becoming increasingly important in applications requiring extended thermal, mechanical, and chemical attributes. Materials which have been tested are magnesium oxide, alumina fiber blanket, pyroceram, and boron nitride. Data obtained are preliminary but suggest an overall uncertainty of ±5% for temperatures above 400 °C.

The HGBOC is a unique device that can measure apparent thermal conductivity of materials with very large temperature gradients (up to 1100 K) or mechanical loads (up to 1 ton). Examples of materials which have been studied in this system are fibrous, multilayer and granular (perlite) insulations. The HGBOC has provided data of use to those modeling the behavior of insulation systems that bear the weight of a cryogenic tank or are subjected to stresses of launch and flight; this applies, for example, to design of components such as fuel tanks for the National Aerospace Plane.

During FY92 we will evaluate several multi-layer insulation (MLI) systems as well as fiber blanket insulations under varying conditions of temperature and fill-gas pressure. Also, individual components of a low-temperature MLI system will be evaluated. These unique tests, funded by the national Superconducting Supercollider (SSC) project, will help determine the optimal thickness of aluminum coating for the low-temperature portions of the MLI system to be used in the SSC. The diffusion of gas through MLI systems also will be studied. Using a medical Nuclear Magnetic Resonance Imager (NMRI), we will map the density of gas between the layers of the MLI as it is evacuated. This is done by imaging the adsorbed gas on the insulation surfaces. If successful, this will be the first experimental determination of the internal pressure of an "evacuated" insulation system.

The Very-Low-Temperature Guarded Hot Plate (VLTGHP) will be used for a number of interesting and exciting measurements next year. A series of foams blown with a candidate CFC substitute (HCFC141b) will be the first materials tested. The VLTGHP will supplement on-going measurements on the Low-Temperature-GHP (LTGHP) apparatus by providing data at lower temperatures than can be achieved with the LTGHP. Data from the two apparatus will be continuous from 4 to 330 K (-270 to +60 °C). This will allow a conductivity-temperature correlation to be developed that should be useful in both aerospace applications and in insulation for domestic refrigeration.

10. Tribology

A.J. Slifka and R. Compos

The High Pressure Liquid Oxygen TurboPump (HPOTP) of the Space Shuttle Main Engine uses bearings made of 440C that run in an oxygen environment. The friction and wear dependance of 440C stainless steel and other HPOTP bearing-candidate materials, with respect to surface velocity, temperature, normal load (or contact stress), and gas environment, is not well known. Knowledge of these relationships is necessary for modelling and determining thermal load and life expectancy in the HPOTP. This investigation is made in an oxygen environment at varying loads (0.5 to 2.0 times the yield strength of 440C), sliding velocities (0.5 to 2.0 m/s), and temperatures (-184 °C, liquid oxygen, to 750 °C).

Tests indicate that over most of the range of speed, load, and temperature there is a tradeoff between friction and wear. Wear rate is a function of the rate of oxidation; when oxides are being formed rapidly, friction is lowered due to the hardness of the oxide layer. Thus, under oxidizing conditions, the wear rate is generally high when the coefficient of friction is low. This tradeoff poses the problem for bearing designers to find the operating conditions where the wear rate is tolerable, and the coefficient of friction is minimized for the wear condition. The data that are being compiled will support such design efforts.

A regime of extreme wear has also been observed in the tests. Under certain conditions, interfacial energy is high enough to cause significant loss of material strength at the sliding interface, but not enough energy is available to rapidly generate a protective oxide layer. This condition leads to both high wear, and high coefficient of friction, and must be avoided in bearing applications of 440C.

During FY91, tests were done in the extreme wear region, using a ball-on-flat test geometry. Tests have begun using ring-on-flat geometry, which will be compared to ball-on-flat results to determine the dependance of the coefficient of friction on the test geometry. In addition to ball-on-flat tests of 440C, ball-on-flat tests are also being done on a wear-resistant, high-silicon stainless steel in an effort to better characterize the thermal conditions at the sliding interface.

An investigation of ion-implanted 440C material has begun, and currently includes nitrogen implanted 440C, and Diamond-Like-Carbon film on 440C. Tests in the future will be done on aluminum and titanium ion-implanted 440C. In the area of ion-implanted 440C, a collaboration between NIST, Dr. Chaudhuri of Tennessee State University, Dr. Wei of Colorado State University, and Dr. Williamson of the Colorado School of Mines continues.

11. Pulse Tube Refrigerator Studies

R. Radebaugh, K. McDermott, P. Storch, E. Marquardt, S. Claunch, and J. Gary

The pulse tube refrigerator is a type of regenerative-cycle refrigerator similar to the Stirling refrigerator but with only one moving part instead of two. As a result, it has the potential for longer lifetimes and lower cost compared with the Stirling refrigerator. Lifetime is a major criterion in satellite based applications where the goal is five years of untended operation for cryocoolers. The lack of moving parts at low temperatures also eliminates most of the vibration that can cause noise in the signal from a cooled sensor. Funding for our work on pulse tube refrigerators in FY91 came from NASA/Ames, SDIO, Kirtland AFB, and Hughes Aircraft. Our efforts in FY91 were concentrated on measuring overall system efficiency, identifying sources of loss, measuring performance of a second stage pulse tube, and improving a version of the orifice pulse tube refrigerator (OPTR) that has no moving parts.

To achieve operation of the OPTR with no moving parts, we proposed in 1987 the use of a thermoacoustic driver (TAD) to replace the mechanical compressor. For this work we established a joint program in 1988 with Los Alamos National Laboratory to utilize their expertise in thermoacoustic drivers and our expertise in orifice pulse tube refrigerators. In October 1989 we succeeded with our first attempt to achieve cryogenic refrigeration with no moving parts in the device we call a TADOPTR. We have designed, constructed, and tested improved components for the device in FY91.

We have proposed using the TADOPTR to liquify natural gas wells that are capped due to remoteness. The thermoacoustic natural gas liquefier (TANGL) burns 20 - 40% of the gas produced to power the liquefier. The liquid would be fed to a liquified natural gas (LNG) tank truck. Our proposal to the Gas Research Institute (GRI) and DoE has been very well received. We have collaborated with John Pellegrino of our division in this proposal; he has proposed the use of membranes to remove water from the natural gas prior to liquefaction. We also have been negotiating with Tektronix regarding a four year program to develop the TADOPTR for use at 10 K to cool superconducting electronic devices. This Defense Advanced Research Projects Agency (DARPA) funded program is expected to begin in early FY92.

Other accomplishments in FY91 include reaching 37 K in one stage and achieving an overall efficiency in a large system about equal to that for a Stirling refrigerator of the same size. A new heat exchanger at the output of the compressor was designed and construction has begun. This new heat exchanger has the potential of improving efficiency further. Problems which remain are the understanding of losses in very small systems and the fluid thermodynamics within the pulse tube.

12. Regenerator Performance

R. Radebaugh, P. Bradley, W. Rawlins, and J. Gary

Regenerative-cycle cryocoolers such as the Stirling, Vuilleumier, Gifford-McMahon, and pulse tube refrigerators make use of regenerative heat exchangers. These heat exchangers operate with oscillating flows and temporarily store the heat being transferred in the heat capacity of the matrix material. Reduction in the regenerator heat loss can lead to a significant improvement in efficiency and in extending the low temperature limit from about 10 to 4 K. Regenerative cryocoolers are of interest to the Defense Department and NASA for the cooling of infrared sensors, and to private industry for cryopumps and magnetic resonance imaging (MRI) systems. This work was supported by NASA/Ames, NASA/Goddard, David Taylor Research Center (Navy), and TRW.

Our regenerator studies include: (1) very low temperature regenerators at 4-20 K, (2) low temperature regenerators at 80-300 K, and (3) regenerator models. In category (1) the matrix heat capacity becomes very small and the major emphasis is on means of increasing the heat capacity by the use of new materials. Most candidate materials have magnetic transitions in this temperature range that give rise to large specific heats. Increasing packing fractions using spherical powders instead of irregular-shaped powders is one method under investigation. We are collaborating with the NIST Metallurgy Division in a program funded by the David Taylor Research Center to obtain and characterize spherical Er_3Ni powder. This material has a high specific heat in the 4-20 K temperature range and is much less expensive than GdRh which has been studied for this use previously.

This year we have made tests with Pb, Brass, and GdRh powders in a regenerator operating in the 8-20 K temperature range. Our results are in reasonable agreement with our third-order model REGEN3, but much different than previous models. The heat capacity of the helium gas in the void volume has an important contribution in this temperature range, which had not been considered before. We also made measurements on a regenerator packed with two sizes of Pb powder to increase the overall packing fraction and increase the total matrix heat capacity while reducing the void volume. The experiments showed improved performance. We are beginning an investigation into coating materials like Er_3Ni onto a screen substrate.

We completed previously a unique test apparatus to study regenerators operating from 80-300 K. In FY91 we designed and constructed a parallel plate regenerator which theoretically should have had a much better performance than existing regenerators. However, measurements of its performance showed an anomalously high ineffectiveness, which we have not been able to explain. A measurement of the ineffectiveness of a stainless steel screen regenerator was also made in FY91 and the results agreed well with our model.

Through our modeling efforts, we have made improvements this year to our REGEN, REGEN2, and REGEN3 computer models that are distributed by Wright-Patterson AFB to U.S. users and developers of cryocoolers. REGEN3 is nearly ready for release in a form designed for running on PC computers. This year we have added several new regenerator materials to the menu selection available in all of the REGEN series of codes. We are continuing our theoretical work on the behavior of regenerators with non-negligible void volumes in the presence of pressure and mass flow oscillations.

Future plans are to investigate the effect of varying the mesh size and cross-sectional area of screens along the length of the regenerator to obtain local optimum conditions. We also plan to study the effect using frequencies as high as 100 Hz.

13. Adsorption Fundamentals and Applications

R. Radebaugh, I. Vazquez, L. Brady, and E. Marquardt

Adsorption of gases on microporous carbon can be used for storing gas and changing the gas pressure in a system by varying the heat input to the adsorber. The technique of varying gas pressure by adsorption is being studied by JPL and Aerojet Electrosystems for use as a heat-driven compressor for gases in a Joule-Thomson refrigerator. The only moving parts in the system are a few check valves that operate once every few minutes. To design these sorption compressors, accurate data are needed on adsorption isotherms.

Our work on adsorption has been funded by the AF Space Technology Center of Kirtland AFB, by NASA/Goddard, and by Aerojet Electrosystems. This year we have made adsorption isotherm measurements on Kr, Xe, N_2, Ar and on a bulk Saran carbon over the temperature range of the normal boiling point to 500 K and at pressures from 0.1 kPa to 3500 kPa. The data on this new batch of Saran carbon agree well with our previous measurements on a sample from a different source.

We have now assembled the world's largest data base regarding the adsorption of low temperature gases on carbon. Such data are ideal for theoretical modeling and correlations. With this large data base we have developed a theoretical correlation that can be used to fit the data from all gases measured on one carbon to an accuracy of ±20% over the entire pressure and temperature range investigated. A different correlation curve fits all the gases on the other carbon sample to within ±30%. This year we have studied the effect of a new carbon sample on the correlation.

Future work is intended to improve the accuracy of the correlation and to determine what properties of the carbon can be used to explain the different correlations for the two different carbons. At present the specific surface area of the carbon and the micropore volume are the only carbon parameters used in the model. Pore size distribution may possibly explain the slightly different correlations for the two carbons.

14. Heat Transfer Surfaces

D.A. Olson and M.P. Glover

In the heat transfer surfaces laboratory we are studying the performance of compact, high-efficiency heat exchangers that are subjected to high heat flux loading (2000 W/cm^2), large internal pressures (7 MPa), and high temperatures (over 800 K). NASA Langley Research Center funded our work this year, Wright-Patterson Air Force Base will sponsor the work of FY92. The heat exchangers we are studying are intended to cool the engine struts of the National Aerospace Plane, which are exposed to the heat generated by the burning hydrogen fuel. Hydrogen gas will enter a cooling jacket heat exchanger at 56 K and 6.9 MPa in the supercritical state, exiting at 890 K and 4.8 MPa. Gas density and transport properties change dramatically from the entrance to the exit due to the large temperature increase.

We tested two compact heat exchangers, one in helium and one with both hydrogen and helium. These specimens were constructed by NASA Langley, and both have a "pin-fin" internal geometry. Pins are formed in nickel plate by photochemically etching the material away from the pins. Because of the high heat fluxes and small flow passages, gas temperatures are not measured directly but are calculated from an energy balance on the gas and specimen. Specimen temperatures are measured with type-N thermocouples welded to the unheated side. Additional thermocouples, mounted using a technique developed jointly with NASA, are used to measure the temperature of the heated surface of the specimen. In this technique, two 0.5 mm diameter holes are drilled side-by-side through the specimen from the insulated side. The holes do not penetrate into the flow channels. A single wire of the type-N pair is mounted in each hole, with the tip welded at the heated surface and a quartz sleeve insulating the remainder of the wire from the specimen. The wires pass out the insulated side of the specimen.

Results of tests on the pin-fin specimens can be compared to past studies of heat transfer in other pin-fin geometries. These studies have been restricted to pin-fins with constant diameter pins over the pin height. Our data agrees fairly well with the results from constant-diameter pin-fins, when we account for heat conduction through the solid pin. The Reynolds number ranged from 450 to 11,400 for the first pin-fin specimen (helium), and for the second pin-fin specimen the range was 1300 to 16,400 in helium and 850 to 14,300 in hydrogen. The effects of variable thermophysical properties of the gas, due to the temperature difference between the specimen wall and the gas, were adequately accounted for as a ratio of the specimen wall temperature to the gas temperature. Helium and hydrogen produced the same non-dimensional heat transfer results, to within experimental uncertainty.

In the future we will test additional heat exchangers and expand the operating range of the apparatus to achieve 350 W/cm^2 heat flux. The NIST facility will be used as a "low heat flux" apparatus to provide reference performance data on heat exchangers which are tested at up to 2000 W/cm^2 at the Wright-Patterson "high heat flux" facility.

15. Fluid Metering

J.D. Siegwarth, J.L. Scott, and M.A. Lewis

A flow facility to provide mass-based data for flowing cryogenic liquid and ambient temperature gas was developed at NIST and has been operated for several years. An ongoing effort to improve metering of natural gas by means of orifice and turbine type flowmeters continued this year. Funded by the Gas Research Institute, this research includes extensive measurements of 5 to 15 cm diameter orifice meters. A specific goal of this research is to provide information that can be used to update standards such as A.G.A. Report No. 3, ANSI/API 2530 and ISO 5167; and in particular, the installation portion of the standards. Our research during 1991 determined that the various piping configurations used in this and other labs to simulate 'good' flow conditions yielded comparable results. An important result this year was our discovery that the location of the pressure taps at the orifice flange can significantly affect the value of the calculated discharge coefficient. We hope to determine whether the results from our 10 cm orifice flowmeter research will translate to other pipe sizes. Work in 1992 will include research with a flowmeter in 15 cm pipe and testing of new types of flow conditioners that are gaining attention. The work in Boulder on gas flow is closely coordinated with similar research on water flow in the Process Measurements Division in Gaithersburg.

Another area of study at the same facility is the measurement of liquid nitrogen flow. We evaluate new measurement techniques and perform special tests on meters to provide measurement traceability to NIST. In conjunction with Calibration Services, we also perform calibrations on commercial meters. The parameters of our calibration test plan are a flow range of 1.26 to 12.7 L/s (20 to 200 gpm), a temperature range of 80 to 90 K (144 °R to 162 °R), and pressures from 0.43 to 0.77 Mpa (62 to 114 psia). In FY91 we performed calibrations or special tests on six cryogenic flowmeters: a vortex-shedding meter, a coriolis meter, and four turbine meters. These meters were calibrated for a manufacturer and supplier of cryogenic fluids and a state government regulatory agency.

In a multi-year program for NASA, we are studying high velocity flows (up to 30 m/s) utilizing water from a local hydroelectric plant to obtain velocities well beyond the range available in any other laboratory. Research has centered around designing vortex-shedding meters. These meters will eventually be used in the ducts of the Space Shuttle main engines. This year we tested a new bluff body shape attempting to provide a more uniform signal as the meter size is scaled. Initial results have been promising and will lead to testing in a Shuttle engine ductwork mockup in FY92.

A new area of flow measurement planned for the nitrogen flow facility involves two phase (liquid-vapor) flow testing. This effort is being funded by NASA's on-orbit fluid management program. Measurement of two phase flow has been a problem for many years, and this new capability, although limited to small flow rates, will provide NIST with a valuable resource for future work.

C. Outputs and Interactions (Chemical Engineering Division)

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3. Patent Awards and Applications

Dubé, W.P., "Thermal Properties Measurement Using a Superconducting Sensor," with J. Moreland (814) and L. Goodrich (814) (Submitted)

Todd, P., "Aqueous Two-Phase Extraction Method for Isolating Ribosomes and Natural Membrane Vesicles," with R.C. Lawson (Outside) (Submitted)

4. Committee Assignments

J. Pellegrino

- National AIChE Separations Division (Director)
  - 1991 Summer National Meeting (Program Coordinator)
  - Separations Division Liaison to DIPPR
- Local AIChE Rocky Mountain Section - Career Guidance Committee Chairman
- University of Colorado Center for Separations with Thin Films (Industrial Advisory Board Member)

R. Radebaugh

- Member of Board for Cryogenic Engineering Conference
- Member of Board for International Cryocooler Conference
- Member of Board for Sixth Temperature Symposium

P. Todd

- NASA LifeSat Science Working Group

5. Other

a. Editorships

J. Pellegrino

- Editorial Board of Gas Separation and Purification Journal

R. Radebaugh

- Advisory Editor for the Journal, Cryogenics

P. Todd

- Co-Editor, "Frontiers in Bioprocessing II," S.K. Sikdar, M. Bier, P. Todd, American Chemical Society Conference Series Vol. 2, 1991
- Associate Editor, Journal of Biochemcial and Biophysical Methods, Applied and Theoretical Electrophoresis

b. Faculty Appointments

J. Pellegrino
Adjunct Professor of Chemical Engineering, Colorado School of Mines, Golden, CO

D. Smith
Adjunct Professor of Physics, South Dakota School of Mines and Technology, Rapid City, SD

P. Todd
Professor Adjoint, Chemical Engineering, University of Colorado, Boulder, CO

c. Collaborations

J. Pellegrino
University of Colorado, Profs. R. Noble and C. Koval, Membrane Transport
University of Colorado, Prof. J. Falconer, Optical Catalyst Probe
Colorado School of Mines, Prof. S. Selim, Thin Film Formation
Chevron Corp (CRDA), Dr. K. Gerdes & M. Hix, Field Test of Acid GAs Permeating Facilitated Transport Membrane
3M Corporation, Dr. D. Gagnon, Composite Film Formation
NIST-Gaithersburg, Polymer Division, Dr. J. Barne, X-ray Evaluation of Membranes

P. Todd
Cell Technology, Inc., Boulder, CO, (CRDA), Electrophoretic and Extractive Isolation of Ribosomes and Natural Vesicles

CHEMICAL KINETICS
AND
THERMODYNAMICS

III. Chemical Kinetics and Thermodynamics Division (833)

Sharon G. Lias, Chief

A. Division Overview

The Chemical Kinetics and Thermodynamics Division is a new Division, created by combining parts of the former Chemical Thermodynamics Division with the former Chemical Kinetics Division at the time of the establishment of the Chemical Science and Technology Laboratory. The merging of NIST programs in these related technical areas had been suggested several times in the past, mainly because the overlap between the two areas of activity is, and has long been, very strong. In particular, both the old Chemical Kinetics Division and the Chemical Thermodynamics Division supported extensive efforts concerned with the compilation and evaluation of data on chemical properties, as well as the estimation of these properties.

Chemical kinetics and chemical thermodynamics are concerned with two aspects of chemical stability. Thermodynamics treats the energetics of chemical transformations with the goal of determining the feasibility or spontaneity of a given process, and further, of knowing the equilibrium yields to be expected for the process. Chemical kinetics is the study of the rates of chemical reactions, the factors which influence those rates, and the detailed mechanisms of the reactions. The two disciplines are strongly interrelated; kinetics uses key concepts of thermodynamics as the basis for interpreting rate data, and kinetic measurements actually provide thermodynamic data. An understanding of the kinetics and thermodynamics of any process involving chemical change is necessary to predict and control the process.

Societal applications of data from chemical thermodynamics and kinetics are numerous and diverse. These include understanding and modeling combustion processes, unravelling the complex effects of pollutants on the earth's atmosphere, and predicting equilibrium properties of processes of interest to technologies varying from power generation and electrorefining to biotechnology. Further, a detailed understanding of the energetics and mechanisms of chemical change are at the very heart of chemistry, and constitute an important goal of science.

The programs of the NIST Chemical Kinetics and Thermodynamics Division include the experimental measurements of kinetic and thermodynamic quantities, the development of measurement techniques and methodologies, the development and certification of Standard Reference Materials, and, perhaps most important, the generation of high quality evaluated data on chemical change, which is disseminated in the form of computerized databases and hard copy publications. An important extension of the latter activity is the formulation of predictive schemes to generate data for the estimation of thermodynamic and kinetic properties.

The focus of Division programs is largely determined by national needs in areas where chemical kinetics and thermodynamics data are important. At the present time, on-going work involves studies relevant to combustion/energy, environmental processes, technology/industrial processes, and analytical chemistry. In each of these areas, both experimental and data compilation/evaluation efforts are underway. Although the applications are varied, most projects are complementary to one another, with for example, data which is evaluated for a combustion database being applied eventually to modeling atmospheric processes, and so forth.

Research activities are driven largely by the needs of the various communities which are served by Division programs, with the Chemical Kinetics and Thermodynamics Division serving as a technical resource for a wide range of external programs. About 35% of Division research is supported by other agencies, notably including the Department of Energy, NASA, the Environmental Protection Agency, and the Department of Defense. In FY91, another 23% and 3%, respectively, of Division work was supported by the Standard Reference Data and the Standard Reference Materials Programs.

Some highly effective Division programs are closely tied to outside activities that both give input to and receive benefit from the NIST work. For example, the NASA Panel for Data Evaluation, which provides the definitive recommendations of chemical kinetic and photochemical data for modeling stratospheric ozone layer perturbations, depends heavily on the work of the Division's Chemical Kinetics Data Center, and includes two Division scientists as panel members. As another example, the Division produces the evaluated database of mass spectra which is required by the EPA for use in EPA contract laboratories. Other work of the Division involves the development of evaluated databases and estimation schemes for the Design Institute for Physical Property Data (DIPPR), a cooperative industrial effort of over 40 companies, institutes and federal agencies sponsored by the American Institute of Chemical Engineers. These activities in support of other programs are an integral part of our mission, and a key means of applying our scientific expertise to industrial, defense, and environmental problems. Moreover, these projects are directly related to, and strongly supportive of, the basic long-range scientific objectives of the Division.

The vitality of Division programs is also evidenced by the large numbers of Guest Researchers and National Academy of Sciences-National Research Council post-doctoral fellowship applications, as well as the leadership positions held by Division members in professional committees and societies. Two Division scientists serve as chairmen of the International Union of Pure and Applied Chemistry (IUPAC) Commissions on Thermodynamics and on Kinetics, respectively, while other Division members are secretaries of committees of those Commissions. Division members are also active on committees of the American Society for Testing Materials (ASTM), the International Council of Scientific Unions Committee on Data for Science and Technology (CODATA), and other committees associated with professional societies. One Division member (S. E. Stein) was chosen as the recipient of a national award sponsored by Exxon Research and Engineering Company for distinguished contributions to fundamental or engineering research on the chemistry and utilization of coal.

Projects currently active in the Division cover a range of subject areas, notably including (1) combustion and energy, (2) environmental processes, (3) technology and industrial processes, and (4) analytical chemistry.

Important projects having to do with combustion and energy include the Department of Energy-sponsored work on refuse-derived municipal waste, the basic research and data evaluation efforts on the kinetics of combustion processes, the award-winning work on coal chemistry, and the basic research on solar energy storage mechanisms, also supported by the Department of Energy.

The Division has a long history of involvement in projects concerned with atmospheric environmental problems. The work on effects of man-made chemicals on the earth's ozone layer, now supported by the National Aeronautics and Space Administration and the Environmental Protection Agency, began in the early 1970's, and has continued to the present with Division members maintaining leadership positions in relevant national and international organizations concerned with such problems. Two Division members serve on the NASA Panel for Data Evaluations, and one is the secretary of the IUPAC Commission on Chemical Kinetics Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Dr. Michael Kurylo, who serves as Acting Director of the NASA Upper Atmosphere Research Program, received the Department of Commerce Silver Medal in October 1991 for research and leadership in this area.

More and more Division research is oriented towards problems related to industrial processes. Current work includes the development of detection techniques for chemical vapor deposition, the exploration of the chemical mechanisms associated with chemical vapor deposition, and the development of a database for dry etching and semiconductor manufacture.

Division involvement with analytical-chemistry related projects goes back many years. Research carried out in these laboratories in the 1960's laid the basis for the development of an analytical technique now called Chemical Ionization Mass Spectrometry; the early research program has evolved into a project now fully funded by the Department of Energy, on mass spectrometric studies of the mechanisms and thermochemistry of chemical ionization processes. Other analytically-oriented work includes the recent development of standard operating conditions for commercial tandem mass spectrometers (MS/MS). The project in the Division which probably has the widest visibility outside of NIST is the maintenance of the NIST/EPA Mass Spectral Database, a large database of electron impact mass spectra which is in use in thousands of analytical laboratories throughout the world.

In addition, Division scientists are active in designing software for the presentation of chemical databases in personal computers (PCs). Because of the difficulty of unambiguously identifying a chemical species, there are special problems involved in building and using databases of chemicals. Division members have provided creative solutions to some of these problems, and as a result the Division is now in the forefront of developmental work on chemical databases in the United States. On-going work is supported by the Environmental Protection Agency, and the Standard Reference Data Program, but proceeds mainly under Division sponsorship with NIST base funding.

A hallmark, and strength, of the activities of the Chemical Kinetics and Thermodynamics Division is the strong tie between experimental, theoretical, and data evaluation efforts. Experimental work encompasses several types of calorimetry, and the determination of reaction rate constants both in the liquid and the gas phases. Other experimental work is aimed at the development of measurement techniques to aid in the detection of reactive intermediate species for kinetic studies, as well as measurement techniques which utilize kinetics for other purposes, such as chemical analysis. Data-centered activities include data compilation and evaluation, applications of data to predictive theories and models, and the formulation of such predictive theories and models. As discussed above, data work also includes the development of software and data handling techniques for chemical databases. The tie between the experimental programs and the data activities is very strong; problems which come to light in the course of data evaluation activities often prompt experimental studies in Division laboratories. The considerable breadth of ongoing experimental activities in the Division ensures that the expertise and insight needed for good data evaluation is available. The theoretical expertise available in the Division supports both experimental and data evaluation work. Most Division scientists are actively engaged in both experimental and data evaluation projects.

The Division is formally divided into three groups, the Experimental Chemical Kinetics Group, the Kinetics Data Centers Group, and the Chemical Thermodynamics Group. The latter Group includes all activities - both experimental and data evaluation - which originated in the former Chemical Thermodynamics Division. In the months since the new Division was created, collaborative ties between members of this Group and the two Groups which originated in the former Chemical Kinetics Division have been formed. In the coming year it is expected that the new Division will be further strengthened by such collaborative outputs.

B. Selected Technical Reports
(Chemical Kinetics and Thermodynamics Division)

1. Optical Studies of Reactive Intermediates

J.W. Hudgens, R. D. Johnson III, and K. Irikura

Resonance enhanced multiphoton ionization (REMPI) spectroscopy provides previously unobtainable data about the electronic structures of a wide variety of free radicals. The procedures used to observe these spectra also lead to sensitive and selective schemes for the optical detection of the radicals. The technique involves tuning an intense pulsed dye laser so that the energy sum of two or three photons of laser light matches the energy of a Rydberg state of the radical of interest. This optical process ultimately generates an ion which is detected by mass spectrometry. Recent work in the REMPI laboratory has emphasized the development of new, sensitive, nonintrusive, laser-based detection methods for radicals that are involved in the dry processing of semiconductor substrates.

Metal halides are products of the reactive etching of GaAs and AlGaAs semiconductor substrates. This year new REMPI detection schemes for AlCl and GaCl were developed. In both species, several new electronic states were observed. In manuscripts currently in preparation the spectroscopic assignments of these new states and the photolytic mechanisms of both species are discussed.

Halogenated methyl radicals are of interest because they are produced by plasmas that etch semiconductors. Many of these radicals are also produced by freons as they degrade in the upper atmosphere or in commercial incinerators. This year the first spectrum of CHF_2 was observed in this laboratory, and a comprehensive analysis of its extremely complex spectrum was made. These new data will support accurate calculations of CHF_2 thermochemical functions.

This year the electronic spectrum of $SiCl_3$ was observed for the first time in this laboratory. The $SiCl_3$ radical is the major chlorosilicon species involved in the chemical vapor deposition (CVD) of silicon films from $SiCl_4$/Ar microwave plasmas. $SiCl_3$ radicals also play important reactive roles during the CVD of silicon carbide films. The REMPI scheme developed for $SiCl_3$ seems capable of sensitively and selectively detecting gas-phase $SiCl_3$ radicals in experiments that seek to measure relative concentrations of $SiCl_3$ during chip processing.

Increasingly, this laboratory employs *ab initio* molecular orbital calculations to provide new insights into free radical structure. For example, this year's scientific papers on the $SiCl_3$ and CHF_2 radicals reported *ab initio* calculations which were used to interpret REMPI spectra and to refine thermochemical values. In the future *ab initio* calculations will be used to predict optical spectra and to help determine the optimum experimental approach for the development of optical detection schemes for specific free radicals.

2. Combustion Chemistry

W. Tsang

The aim of this program is to develop a fundamental quantitative understanding of high temperature reactions of organic compounds so that large scale phenomena can be fully described in terms of elementary thermal reactions. Experimental investigations are carried out in a unique heated single pulse shock tube. Selection of specific systems for study is largely guided by an affiliated data evaluation effort (see below), with an emphasis on obtaining results which are needed to develop and validate correlation schemes for the prediction of rate expressions.

An important thrust during the past year has been the investigation of the kinetic properties of resonance stabilized radicals such as the allyl and propargyl radicals. Resonance stabilized organic radicals play an important role in the chemistry of organic systems at high temperatures because their long thermal lifetimes enable them to survive to undergo a variety of reactions.

The suggestion has been made by Dr. Stephen Stein of this Division that propargyl radicals may be an important precursor of aromatic products leading to soot formation in combustion systems. The reasoning was that because propargyl radicals have no weak beta C-H bonds, at high temperatures they can only recombine, leading to the formation of benzene. In experiments at 1000-1200 K, the first direct proof of this important reaction channel - the formation of large yields of benzene from reacting propargyl radicals - was obtained. In addition, large quantities of fulvene and other C_6H_6 isomers were also detected. Similar studies of allyl radicals led to the determination of the rate expression for the decomposition of the allyl radical to allene, and a new and more accurate determination of the heat of formation of the allyl radical.

With the support of the Department of Energy, new experiments in liquid phase pyrolysis have been initiated. The aim of this work is to develop a more fundamental understanding of the mechanism of dioxin formation during incineration processes. Apparatus for carrying out such studies has been constructed and is being tested. Initial studies of reactions in phenol and o-chlorophenol have led to the identification of products formed at temperatures near 400 °C. Detailed mechanistic studies will be carried out and the effects of inhibitors and catalysts will be determined. Results will be compared with those from experiments in the presence of fly ash.

The incineration of chlorobenzene and tetrachloroethylene in typical organic fuels was modelled in collaboration with D. Burgess of the Process Measurements Division. The results showed that the stoichiometry of the processes was important. Failures of incineration are largely because of problems with mixing. Incinerability rankings, which are widely used in the licensing process, are related to the parameters that govern the stability of compounds under pyrolytic conditions.

3. Carbon and Coal Chemistry

S. E. Stein

The significant findings of this research program, which is fully supported by the Gas Research Institute (GRI), were distilled and highlighted for a broad audience in an invited review published this year in "Accounts of Chemical Research".

Two other articles describing recent results appeared during the year. In one, a quantitative analysis of the chemical properties at the edges of very large polycyclic aromatic arrays was presented, and implications for carbon chemistry discussed. In a paper published in "Nature", an analysis is made of the relative stability of precursors to graphite and diamond. It was shown that thermodynamics invariably favors graphite precursors.

The results obtained in this research program during the past nine years were recognized by the American Chemical Society by the selection of the principal investigator as the 1992 recipient of the Henry H. Storch award in Fuel Chemistry.

4. Solar Energy Conversion and Storage

P. Neta

A project fully supported by the Department of Energy examines fundamental chemical processes related to solar energy storage.

Metalloporphyrins may serve as efficient photosensitizers for solar energy conversion and storage. This is due not only to their broad absorption spectra in the visible light range but also to the rich redox chemistry of the various metalloporphyrins. Experiments are designed to elucidate individual steps in reaction mechanisms pertinent to the conversion of solar energy into chemical energy.

Pulse radiolysis and laser flash photolysis techniques are used to study the kinetics and mechanisms of reactions important in the catalytic oxidation of water to oxygen and reduction of water to hydrogen, utilizing metalloporphyrins as photosensitizers. After having established the important parameters that control such systems in earlier stages of this project, experiments designed to couple the reduction and the oxidation halves of the system were initiated this year. The approach is to use a redox pair, such as quinone/hydroquinone, where quinone may serve as the oxidant in one half of the system while its product, hydroquinone, serves as reductant in the other half of the system.

Metalloporphyrins with transition metal centers may catalyze various reductions and oxidations through different oxidation states of the metal center. Since reduction and oxidation of the metalloporphyrins themselves may take place on the ligand or on the metal center, and since only the latter are useful for catalysis, an investigation was made of structural and medium effects on the path of electron transfer in several metalloporphyrins. Results on Ni- and Cr-porphyrin revealed the importance of porphyrin structure, substituents, metal center, and axial ligands on the path of electron transfer. A study of reduced Ni-, Cr-, and Fe-porphyrins reacting with radicals that lead to formation of metal-carbon bonds, has been initiated. These species may play an important role in catalysis.

5. Aqueous Free Radical Kinetics

R.E. Huie and P. Neta

This work includes studies of the reactions of inorganic radicals and of organic peroxyl radicals in solution. The former are of interest because of their possible role in the environment and for industrial chemistry, while the latter studies have led to information which helps in understanding the biological activity of these radicals.

Accomplishments during the past year include the determination of rate constants for reaction of inorganic radicals (derived from sulfate, carbonate, chloride, hypochlorite) with various reactants, the effects of temperature and solvent, and the determination of redox potentials (for $CO_3^{\cdot -}$, $SO_4^{\cdot -}$, $ClO\cdot$). For example, from the temperature dependences of the reactions of the carbonate radical, $CO_3^{\cdot -}$, with alcohols and one cyclic ether it was found that the reaction mechanisms are more complicated than previously believed, involving an interaction of the radical with the -OH or -O- group rather than simple hydrogen abstraction. The temperature dependence of the reactions of the dichloride radical, $Cl_2^{\cdot -}$, with unsaturated compounds in aqueous and aqueous acetonitrile solutions were strongly affected by the solvent composition; for example, the activation energy of reaction with 2,3-dimethyl-2-butene changes from positive at high concentrations of acetonitrile to negative at low concentrations. In the study of borate-persulfate solutions at high pH, laser flash photolysis results demonstrated that earlier conclusions that the borate radical was formed were incorrect; the observations which had been attributed to the borate radical were in fact traceable to the carbonate radical.

The second part of this work is concerned with peroxyl radicals that may be produced in biological systems, in particular from chlorofluorocarbons, and which may have deleterious effects. During the past year, the combined effects of temperature and solvent on the rate constants for oxidation of several organic compounds by chlorinated peroxyl radicals were thoroughly studied. The activation energy and the pre-exponential factor tended to increase or decrease together as the solvent composition was varied; that is, the variation in rate constant was the result of two compensating effects. These results suggest that electron transfer from organic reductants to chlorinated methylperoxyl radicals takes place by an inner sphere mechanism involving a transient adduct of the peroxyl radical to the reductant. The effects of the structure of fluorinated alkylperoxyl radicals on reactivity were also examined.

6. Stability of Halocarbons in the Atmosphere

M. J. Kurylo, R. Huie, T. J. Buckley, W. Braun, and A. Fahr

This program, supported by NASA and EPA, focusses on the measurement of the gas phase kinetic and photochemical parameters for industrial chemical compounds that can play an important role in atmospheric chemistry. The research emphasizes those processes that relate to our understanding of the fate of natural and anthropogenic trace gases in the troposphere and their chemical role in the stratosphere. Major goals of this work include predicting the impact of human activities on stratospheric ozone and on global climate.

Recent laboratory accomplishments include flash photolysis-resonance fluorescence measurements of the rate constants for the reactions of OH radicals with compounds being developed by the chemical industry as possible CFC (chlorofluorocarbon) alternatives. The studies on the reactivity of halogenated alkanes toward OH have been continuing, and a new effort on the reactivity of fluorinated ethers has been initiated. Room temperature results indicate that several of the proposed fluorinated ethers have tropospheric lifetimes in the range to make them viable CFC replacements.

In other studies, the reactivity of HCFC-141b was re-investigated under conditions where secondary reactions would be minimized. We have found a lower rate constant than previously reported, resulting in a longer calculated atmospheric lifetime.

To assess the effect of halocarbons on the stratosphere, accurate ultraviolet cross sections are needed. At the longer uv wavelengths, the cross sections are very low but, since the light flux is much higher, absorption in this region can be important. Measurements of such low cross-sections are difficult and unreliable. A new method has been developed which combines measurements of the gas phase cross sections with measurements made in the liquid phase to extend the range over which accurate values can be determined. The method minimizes some of the systematic errors that accompany the measurement of extremely low gas phase absorbtivity in the ultraviolet, and can potentially be used over a wide range of temperature.

A kinetic modeling program for analyzing complex, multi-component systems has been written and tested by comparing the time dependence of processes involving HO_2 and CH_3O_2 radicals. The time dependence of the ultraviolet absorption of these radicals, as measured in the laboratory, was compared to the time dependence predicted by the model to obtain the best fit to various kinetic parameters. This approach has been used to optimize experimental design and obtain best values for rate constants and absorption coefficients.

Finally, in collaboration with researchers at the Ford Motor Company, an investigation has been carried out on the reactivity toward OH of potential fuel additives for internal combustion engines. We have measured the temperature dependence for the reactions of OH with *tert*-amyl methyl ether and with di-isopropyl ether. The latter results did not show simple, linear Arrhenius behavior. At high temperatures, this is probably due to the onset of abstraction from the less reactive CH_3 groups. These results are important both for assessing the impact of these compounds on photochemical smog formation and for determining the mechanism of their action in the combustion chamber.

7. Standardization of Tandem Mass Spectrometry

R.I. Martinez

The major accomplishment of this project in previous years has been the development of a standardized tuning protocol for commercially-manufactured tandem mass spectrometers (sometimes called MS/MS instruments), which are widely used in analytical chemistry for collisionally-activated dissociation (CAD) of ions. The use of this protocol permits the generation of instrument-independent CAD spectra, a goal long thought impossible by the practitioners of the technique; the operating conditions must be selected so that the spectrum represents the initial collision-induced fragmentation of the subject ion. This is possible only under "single-collision" conditions, i.e., conditions under which the ions selected for analysis undergo only a single collision in the dissociation chamber. An international round robin conducted in 1988-89 established the validity of this standardized tuning protocol.

During the past year, the EPA requested that the standardized MS/MS tuning protocol be formulated for incorporation into an EPA Test Method. The Test Method will be included in U.S. EPA SW-846 Laboratory Manual of Test Methods, and will be used for Quality Assurance/Quality Control, Instrument Performance Certification, and Operator Proficiency Testing of CAD measurements in MS/MS instruments which use rf-only multipole collision cells. The protocol will impact on a large community, since there are more than 500 such instruments now in operation, representing a capital investment of more than $200 million.

The EPA Test Method is based on the NIST standardized MS/MS tuning protocol as well as the absolute product distributions for the fragment ions formed by the CAD of the acetone molecular ion as a function of the center-of-mass collision energy E_{CM}. The shapes of these CAD breakdown curves are very similar to those of the corresponding breakdown curves obtained from photoelectron-photoion coincidence experiments, in which the internal energy of the dissociating ion is well-defined. Using these data, it was possible to estimate the extent of energy transfer as a function of the center-of-mass energy for the CAD of the acetone molecular ion. The data may indicate that when there is a significant gap between the ground state and first excited state of an ion, a fraction of the collisionally-activated dissociation events may occur from an excited state of the ion, in good agreement with conclusions from other studies.

8. Chemical Database Development

S.E. Stein, W.G. Mallard

The Division has an active program for the development of software for use with chemical databases. Because of the difficulty of unambiguously identifying a chemical species in a database, there are special problems involved in building and using databases of chemicals. The Division program has provided creative solutions to some of the generic problems associated with building chemical databases. For example, software and procedures developed in this project permit, for the first time, the use of the chemical structure rather than the Chemical Abstracts Registry Number as the primary identifier of a compound in a database.

During FY91, the software known as "Structures and Properties", designed by S. E. Stein, was released for distribution to the public. The software, a spin-off of software originally developed for the mass spectral database, includes structural and sub-structural searching for data associated with species drawn on the screen by the user. The software also generates estimated values of molecular properties (heats of formation, vapor pressures, boiling points) for the molecules drawn on the screen; this is done using a complete implementation of Benson's Group Additivity method, including all of the ring corrections, automatic perception of symmetry numbers and determination of various other non-bonded interactions. This represents a considerable programming challenge, and has never before been fully implemented to our knowledge. The software also allows the user to create balanced chemical reactions and automatically computes equilibrium constants from 300 to 1500° K. The product has attracted much attention from potential users/distributors and various industrial laboratories. During FY92, the software will be adapted for use with other existing in-house databases.

During the year, Version 3.0 of the NIST Chemical Kinetics Database was released. This database, designed by W.G. Mallard, provides a tool for rapidly retrieving rate constant data on a particular reaction, all of the reactions of a given species, or all the data reported in a given literature reference. The database developed for use on personal computers includes a graphic display of the temperature dependences of reaction rate constants, and software to enable a user to evaluate the data. To date, several hundred copies of the PC product have been sold by the Standard Reference Data Program. The 1991 update contains over 16,800 records relating to over 7400 reactions (5800 reactant pairs), an increase of 5,000 records. The total number of chemical species treated in the database has increased from 2,400 to 2,800. In addition to adding data, the database programs were modified to add features that make the database more useful.

A database of chemical names, registry numbers and formulas has been prepared from a large number of available computer data files. This database contains over 200,000 different substances and more than 450,000 chemical names. It also has approximately 60,000 chemical structures from the Mass Spectral Database and other NIST structure files. This database is a valuable resource for all future data activities in the Chemical Science and Technology Laboratory.

9. Chemical Kinetics Data Evaluation: Combustion, Manufacture of Semiconductor Devices, Environmental Processes

W. Tsang, J. Herron, R. F. Hampson, and D. Frizzell

A long range program in the Chemical Kinetics Data Center is directed at producing a complete database of self-consistent, evaluated kinetic data for use in the modeling of hydrocarbon combustion. The evaluation of thermal rate data important for combustion phenomena is closely tied to a related program of experimental studies described above under the heading "Combustion Chemistry".

Work to produce an evaluated database covering all data pertinent to combustion of the C_1-C_4 alkanes and methanol was continued this year with support from the Department of Energy. Earlier publications dealt with reactions involving methane, methanol, propane, n-propyl and isopropyl radicals, isobutane, t-butyl and isobutyl radicals, propene and allyl radicals. Over the past year an evaluation of the data on reactions of 2-butene resulted in the resolution of a long standing problem in the interpretation of these data.

In related work, an analysis of experimental results on the unimolecular decomposition of organic radicals at low pressures was made in collaboration with Professor Gutman of Catholic University. A paper on neopentyl radical decomposition has just been published. Energy transfer parameters for collisional deactivation by He, Ar and N_2 at 600 K are similar to those found for ethyl radical decomposition. The existing data also suggest that the temperature dependence of this process is greatest for an atom and decreases with the increasing complexity of the collision partner.

The information about these general trends, which are in line with our deductions for alkane decomposition and radical combination reactions, contributes to the body of reliable data on the energy transfer parameter which will be needed to estimate kinetic data for these processes.

The other two quantities that determine unimolecular behavior are the A-factor and activation energy for decomposition. For the series n-propyl, isobutyl and neopentyl the A-factors are essentially constant except for reaction pathway degeneracy, a trend observed previously for the alkanes. However, in the case of the alkyl radicals, the activation energies are also constant, and thus methyl substitution has no effect. This may be a consequence of an increase in pi bond energy which compensates for the substituent effect.

In a closely related effort, we continue to provide evaluated data for the simulation of propellant chemistry. The second part of our review on propellant decomposition has been accepted for publication in the Journal of Physical and Chemical Reference Data.

The Chemical Kinetics Data Center provides the NASA Panel for Data Evaluation with evaluations for the chemical kinetics of atmospheric reactions involving halogenated species. For each reaction, a recommended rate constant value with a measure of its reliability and supporting documentation is provided. Paralleling this activity, Division personnel are members of the IUPAC Commission on Chemical Kinetics, Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Here they have primary responsibility for evaluation of the chemical kinetic and photochemical data for reactions of halogenated species and selected oxygenated species. An updated and expanded evaluation of chemical kinetics and photochemical data for use in modeling calculations of the earth's atmosphere was completed this year for IUPAC, and has been submitted for publication in the Journal of Physical and Chemical Reference Data.

Work continues on the evaluation of data related to modeling the complex chemistry encountered in the manufacture of semiconductor devices. The preliminary data evaluation work focusses on the elementary single step chemical reactions initiated by breakdown of SF_6. The approach is the same as that used to provide a database for modeling combustion chemistry; every possible reaction of every possible species is being considered, and for every reaction, a rate constant is assigned. The most important output of this year's work is our reanalysis of the thermal decomposition of SF_6 which led to a new value 420 kJ mol^{-1} for the strength of the S-F bond. This is an increase of 20 kJ mol^{-1} and has important implications regarding the stability of the SF_5 radical and the chemistry of SF_6 decomposition systems. This is potentially of great importance since SF_6 is widely used in switching equipment in the electric power industry, and its breakdown product, S_2F_{10}, is highly toxic.

10. Ion Energetics Database

S.G. Lias, R.D. Levin, and P. Ausloos

During FY91, work proceeded on the production of a major update to the personal computer version of the recent Data Center monograph, "Gas-phase Ion and Neutral Thermochemistry". The database product currently distributed by the Standard Reference Data Program consists of two separate databases, one giving thermochemical data for positive ions (ionization energies, appearance energies, proton affinities) and one for negative ions (electron affinities, gas phase acidities). In the update, these two files will be combined into a single PC database which will use the search software called "Structures and Properties", described above under the heading Chemical Database Development.

The current Positive Ion Energetics database does not include any original references before 1982, and the unevaluated data from which the evaluation was made are not displayed; the update will include all references and all data points. The literature from the years 1987-1990 has been abstracted and entered into the computer file. In the update, structural diagrams of molecules will be included in the distributed database for the first time. New search modes will also be implemented, such as retrieval by Registry Number, and by ionization energy. This work is being carried out in collaboration with Dr. Stephen Stein.

The Negative Ion Database was kept up-to-date during FY91 by the addition of all new data appearing in the literature, and plans were coordinated for entry of these files into the update.

Data on the energetics of ionic clusters have been entered into a database, and are now being evaluated in collaboration with Dr. Michael Mautner. A computer database, and a publication in the Journal of Physical and Chemical Reference Data will result.

11. The NIST/EPA Mass Spectral Database

S.E. Stein, P. Ausloos, C. Clifton, and R.I. Martinez

This Data Center was created three years ago for the purpose of maintaining, updating, and improving the NIST/EPA Mass Spectral Database, a computerized collection of electron mass spectra which is one of the most widely-known products of NIST, in use in thousands of commercial mass spectrometers. The database was originally put together at EPA and NIH, and starting in 1978, was distributed by the Standard Reference Data program while still being maintained by the EPA. In 1987, a fully searchable personal computer version of the database was developed at NIST. In late 1988, the primary responsibility for the maintenance, evaluation and updating of the database was moved to NIST from EPA.

Data Center activities focus on improving the mass spectral database, with respect to both quality and size, and on the development of improved software for searching, matching unknown spectra, and locating/correcting errors. The database now includes, in addition to the spectra, data on the structures of nearly all the relevant molecules as well as some auxiliary data on retention times. Attention is also given to expanding the focus of the project to include other data such as infrared spectra of use for analytical chemistry.

When the database was transferred to NIST in late 1988, it contained numerous errors. A systematic effort has been made to locate and correct or eliminate incorrect spectra. This continuing work involves both the use of algorithms to pin-point errors in the database, and a spectrum-by-spectrum evaluation by expert mass spectrometrists. During 1991, a major focus was the manual evaluation of all replicate spectra in the collection in order to provide an auxiliary file of replicate spectra by the time of the next release. Statistical analyses of the probability of retrieving a correct spectrum from a large database have demonstrated that the inclusion of replicates substantially improves the performance of a database. The file of replicate spectra will include more than 10,000 spectra.

During 1991, a major thrust was initiated to obtain new spectra for the database. Activities included both the determination of original spectra in-house, collaboration with other laboratories such as Aldrich Chemical Company and NIH who can provide spectra of important compounds, and the solicitation of collections of spectra from industrial laboratories. As a result of these activities, the next update of the database in May 1992 should include about 75,000 spectra (including replicates), an increase of 20,000 spectra since the last release in April 1990.

12. Fluorine Bomb Calorimetry

P.A.G. O'Hare

An international effort, spearheaded by this laboratory, has resulted in significant advances in the understanding of the thermodynamics of tungsten ditelluride, WTe_2, a compound which is used as a high temperature lubricant and in photovoltaic cells. A highly pure sample of WTe_2, synthesized by Professor G. Hope (Griffith University, Brisbane, Australia) was studied by the technique of fluorine combustion calorimetry. The specific energy of combustion yielded the standard molar enthalpy of formation with a precision several times smaller than the result that, hitherto, had to be estimated from high-temperature vaporization studies. Part of this sample was given to Professor R. Weir (Royal Military College of Canada, Kingston, Canada), who determined the low-temperature heat capacity and, thence, the standard entropy. Results of this joint collaboration have been submitted for publication. Another part of the WTe_2 specimen has been sent to Professor Cordfunke (ECN, Petten, The Netherlands) to determine the high-temperature enthalpy increments and the heat capacity. In the course of the NIST investigation, the standard molar enthalpy of formation of TeF_6 was also determined.

A collaborative study with Dr. S. Susman and colleagues (Argonne National Laboratory) of the thermodynamic properties of vitreous (glassy) chalcogenides has, among other results, produced evidence for the presence of significant levels of impurities in a secondary thermochemical standard, rhombohedral sulfur, which, hitherto, had been considered ultra pure, and had been used in a number of key thermochemical studies. The NIST fluorine-combustion work on this sample has led to the conclusion that the published standard enthalpy of formation of SF_6(g) should be adjusted by ≈ 0.5 $kJ \cdot mol^{-1}$, and it may require a minor change, ≈ 0.3 $kJ \cdot mol^{-1}$, in the critically evaluated enthalpy of formation of aqueous sulfate ion.

A review article on the present status and the future of fluorine combustion calorimetry was coauthored with Dr. V. Ya. Leonidov (USSR Academy of Sciences, Moscow, U.S.S.R.), and is now in press.

Plans for FY92 include thermochemical studies on the following systems: crystalline and vitreous GeS_2; WSi_x, where $x = 2.0$ and 1.96; and $MoSi_{1.96}$. Although the other vitreous germanium chalcogenides can be synthesized rather easily with the desired stoichiometry, such is not the case for the disulfide. Therefore, the measurements will not only provide the enthalpy of transition, they will, in addition, give an indication of the reproducibility with which high-purity batches of vitreous GeS_2 can be prepared. Our interest in the silicides arises from their use in integrated circuits, and the almost complete lack of reliable thermodynamic information on them.

13. Precision Oxygen Bomb Calorimetry

D.R. Kirklin

Precision bomb calorimetry provides the data necessary to calculate precise and accurate enthalpies of formation, which are necessary to evaluate the molecular energetics of important materials and the thermodynamic feasibility of their chemical reactions. The NIST bomb calorimetry laboratory has a unique adiabatic aneroid calorimeter which is well characterized and makes combustion measurements on solid samples of 100-300 milligrams. It can be operated as a static or rotating bomb calorimeter. The capability of handling samples of small size has allowed routine measurements on samples of high purity materials that were available only in small quantities.

During the past few years the NIST bomb calorimetry laboratory has developed techniques which have made it the only laboratory that is presently making precise and accurate measurements on organic phosphorus and strained organic compounds. Many of the novel materials of interest today are only available in extremely limited quantities, so new calorimetric procedures have been developed to permit measurements on samples weighing only 10-15 milligrams.

During the past year, we have collaborated with a group located at Drexel University and the University of Pennsylvania that has developed methods to prepare and purify fullerenes. This collaboration led to preliminary calorimetric measurements on a 99% pure sample of C_{60}. These preliminary results, presented at an international fullerite workshop at the University of Pennsylvania on August 2-3, 1991, appear to be the first reported thermodynamic measurements on C_{60}.

Measurements will be performed during fiscal year 1992 on high purity samples of some novel materials that are only available in limited quantities. A high purity sample of the fullerene, C_{60}, has been received from Drexel University and the measurements will be completed in the near future. A 120 mg sample of the strained organic compound, cubane monocarboxylic acid, is being purified so that it can be investigated during this year to provide a better understanding of the strain energy of these important compounds.

In addition to the measurements on the novel compounds of interest, materials will be investigated which are available in large quantities and high purity. The most important project in this class will be the certification of a new batch of the NIST calorimetric standard (NIST SRM 39i), benzoic acid. In addition, the NIST adiabatic, aneroid bomb calorimeter will be used in the rotational mode to provide reliable calorimetric data on key organic phosphorus compounds. These data are needed to develop a reliable estimation scheme for large numbers of organic phosphorus compounds on which it would be very difficult to perform critical measurements due to their hazardous properties.

14. Bomb Calorimetry for Biotechnology

E.L. Diaz, E.S. Domalski, and D.R. Kirklin

The enthalpies of combustion of crystalline glycylglycine and DL-alanyl-DL-alanine were determined using oxygen bomb calorimetry. The enthalpies are based upon the amount of CO_2 produced in the combustion reaction rather than upon the sample masses because of uncertainties in the moisture contents of the samples. The corresponding molar enthalpies of formation for glycylglycine and DL-alanyl-DL-alanine, as well as of glycine ($-CH_2NHCO-$) and DL-alanine ($-CH(CH_3)NHCO-$) repeating units for peptides in the crystalline state, were also derived.

The usefulness of data for such repeating units can be shown by example calculations for estimating the enthalpy of formation at 298.15 K of crystalline DL-alanylglycine and glycyl-DL-alanine. Combining the repeating unit for DL-alanine with the enthalpy of formation of glycine, $(-248.6 \pm 2.1) + (-528.5 \pm 0.5)$ kJ mol^{-1}, gives the estimated enthalpy of formation of DL-alanylglycine, -777.1 ± 2.2 kJ mol^{-1}. This value compares very well with the corresponding experimental value of -776.9 ± 0.8 kJ mol^{-1}. Using a similar approach, the enthalpy of formation of glycyl-DL-alanine can be calculated; $(-219.5 \pm 1.4) + (-562.0 \pm 1.0)$ kJ mol^{-1}. Experimental data for $\Delta_f H^\circ_m$ are not available for the comparison of this dipeptide. The paper which describes this work has been approved by WERB and will be submitted to the Journal of Chemical Thermodynamics.

Another paper which describes research on the enthalpies of combustion of three nucleosides, has been completed and will be submitted soon for internal review.

15. High Temperature Heat Capacity Measurements

D.A. Ditmars

Highly-precise and accurate heat capacity calorimetry of non-reacting systems determined at high temperatures (300 - 1500 K) have the following applications: (1) to provide accurate values for thermodynamic functions (H, C_p, S, G) of the elements and inorganic compounds for which current information is uncertain due to conflicting or unreliable data, (2) to create and expand a database of accurately-known thermodynamic properties for selected elements and compounds widely used in the calibration of differential scanning calorimeters (DSC's), and (3) to determine accurate high temperature heat capacity values for important substances, such as high-T_c oxide systems.

Precise data on the enthalpy of fusion of indium was provided to the Standard Reference Materials (SRM) Program so that the SRM certificate could be prepared and indium could be issued as a standard sample for the calibration of DSC's. Heat capacity and enthalpy of melting experiments on aluminum, between 933 and 983 K, were also completed.

During FY91, internal publication approval was received on the manuscript: "Determination of the Electronic Density of States of $YBa_2Cu_3O_{7-\delta}$, with authors M.E. Reeves, D.A. Ditmars, S.A. Wolf, and T.A. Vanderah. This study was carried out in cooperation with researchers at the U.S. Naval Research Laboratory.

A manuscript is in preparation on the enthalpy and temperature of melting of tin. As with indium, these data on tin are important for the calibration of DSCs.

16. Metals Content of Combustible Municipal Solid Waste Components

K.L. Churney and E.S. Domalski

Information on the sources of minor and trace amounts of metallic elements in the combustible components of municipal solid waste (MSW) can be used to direct changes in the chemical production and modes of discard of materials or substances in order to minimize or eliminate undesirable metals or their compounds from the waste stream. This could result, for example, in dramatic improvements in the quality of emissions from incinerators and related combustion facilities. A research project aimed at determining the metals content of combustible municipal solid waste was sponsored by the Department of Energy Waste Materials Management Division.

From an earlier study on the chlorine content of the combustible components of municipal solid waste, funded by the Department of Energy, large quantities of separated and milled combustible components from the Baltimore County Resource Recovery Facility and from the Greenpoint Incinerator in Brooklyn, NY, had been stored under refrigeration and were available for the study. The analytical results have been examined and evaluated. Tables of data have been prepared, and the results have beem summarized. A final report for the sponsor and a journal article are being prepared.

The results showed that the day-to-day variability in the metal content of any particular component of MSW can be high. For example, for a five day period of study, Ni in the paper fraction was below the detection limit of 5 ppm for days 2 and 5, was near 10 ppm for days 1 and 4, and was 6810 ppm on day 3.

17. Phase Change Calorimetry

T.J. Buckley and K.L. Churney

Schemes for reliably estimating heats of formation, which are essential to cut development costs in the chemical industry, are based on values for enthalpies of formation of key compounds in the gaseous state at 25 °C. To obtain such values, a capability for determining enthalpies of sublimation/vaporization is being developed so that combustion bomb calorimetry measurements of solids and liquids can be used to derive gas phase data. Since key compounds can be costly to synthesize, the enthalpy of sublimation apparatus and the bomb calorimeter were selected for their applicability to research (milligram) quantities of material.

An apparatus for determining vapor pressure as a function of temperature has been constructed. This apparatus has been performance tested in the range between 1 to 10^{-3} torr and from 25 to 125 °C, and has been re-designed and re-built to eliminate problems identified during the tests.

Auxiliary thermodynamic data, such as enthalpies of fusion, heat capacities, and purity determinations are needed to obtain reliable enthalpies of combustion. A scanning calorimeter, automated during the previous year, was used to obtain preliminary heat capacity measurements for three intermetallic compounds (Cu_3Sn, Ni_3Sn_4, Cu_6Sn_5) that are of importance to the computer industry in general, and the military establishment in particular.

18. Thermodynamics of Aqueous Electrolytes

D.G. Archer and D.B. Neumann

A new database of aqueous thermodynamics, now called AQ, has been prepared for the chemical engineering community by D.B. Neumann. The database includes the thermodynamic properties, especially activity coefficients of solutes and osmotic coefficients of the solvent, of single and mixed electrolyte solutions over a temperature range from 0 °C to 200 °C and concentrations up to 12 molal and higher. These properties find applications in a variety of areas, from geochemistry to biotechnology, which require the chemical equilibrium thermodynamics of aqueous solutions and/or the calculation of speciation in such solutions in heterogeneous phase equilibria. Accurate, reliable, and consistent thermodynamic data, including Gibbs energies and/or equilibrium constants, activity and osmotic coefficients, and heat capacities, are required for such calculations. In fact, the results of equilibrium calculations for aqueous systems can only be as good as the thermodynamic data available, and in many instances results of equilibrium calculations are highly sensitive to the values of the thermodynamic input data.

With this need for reliable data in mind, the Aqueous Electrolyte Data Center has, over the last three years, worked with the Design Institute for Physical Property Data, DIPPR, to develop the AQ database. The primary capabilities of AQ are that it can calculate and then tabulate or graphically display the activity coefficients ($\gamma_\pm$) of solutes and the osmotic coefficient (φ) of the solvent for aqueous solutions of pure and mixed electrolytes as a function of concentration and temperature. It also provides annotation regarding ranges of validity and reliability. As a result, more than 900 parameterized equations, as well as some purely tabular data for over 350 binary aqueous electrolyte solutions, are now stored in the AQ database. The completed package is now under review by the contractor.

In a study of the thermodynamic properties of the $NaCl+H_2O$ system carried out by D. G. Archer, the available experimental thermodynamic data for NaCl(cr) were fitted in order to generate thermodynamic values as a function of temperature, for a nominal pressure of 0.1 MPa. Thermal measurements (heat-capacity values and enthalpy-increment values) were fitted with a new method. Equations that describe the thermodynamic properties of the NaCl + H_2O system were obtained from the fit to experimental results. The experimental results included in the fit spanned the temperature range of approximately 250 to 600 K and, where available, the pressure range from the vapor pressure of the solution to 100 MPa. The work includes new equations and/or values for the following properties: (1) $\Delta_f G_m°$ and $\Delta_f H_m°$, for formation from the elements, for NaCl(cr) and $NaCl{\cdot}2H_2O$(cr) for 298.15 K and 0.1 MPa; (2) the change in chemical potential for both NaCl and H_2O in NaCl(aq) as a function of temperature, pressure, and molality, valid from 250 to 600 K and, where available, from the vapor pressure of the solution to 100 MPa. The results are to be published in the Journal of Physical and Chemical Reference Data.

19. JANNAF Thermochemical Tables for Species of Importance to Ozone Depletion

D.B. Neumann

The goal of this project, being carried out in collaboration with Malcolm W. Chase of the Standard Reference Data Program, is to provide NASA with a comprehensive evaluation of the thermodynamic data for stable as well as transient species involved in the network of reactions related to the destruction of ozone in the upper atmosphere. The set of gas phase species evaluated in FY1991 includes:

OH, OH_2, HCl, HOCl, HOClO, $HOClO_2$, $HOClO_3$, ClNO, $ClNO_2$, ClONO, $ClONO_2$

At the present time the annotated bibliographies for the species have been assembled and the relevant data have been extracted for all the species of interest. Due to various reaction networks, or pathways, experimental thermodynamic data for a number of the species are closely related to the thermodynamic properties of several of the species evaluated in the previous fiscal year. Data summaries of the relevant thermodynamic and spectroscopic data have been written for eight of the eleven species under the current program.

Summary versions of the thermodynamic tables in JANAF format, for the eight species studied in FY90, have recently been published: Abramowitz, S.; Chase, M. W.; "Thermodynamic Properties of Gas Phase Species of Importance to Ozone Depletion"; Pure Applied Chem.; 63, 1449-54 (1991). The complete tables with their documentation have been submitted for publication in the Journal of Physical and Chemical Reference Data.

In FY92, the thermodynamic tables for these 11 chlorine cycle related species will be submitted to NASA, and a manuscript will be prepared for publication in the Journal of Physical and Chemical Reference Data. A similar study on the relevant bromine containing species will be initiated.

20. Thermodynamics of Organic Compounds

E.S. Domalski and S.E. Stein

Work was initiated on the compilation of a comprehensive database of enthalpies of formation of organic compounds. The plan is to quickly collect as much as possible of the existing relevant literature, and enter the data into a computer database. This database will be made available as a searchable computer product, and (probably) as a hard copy publication. Organometallic compounds will be included in this compilation.

The on-going collection of data on organic thermochemistry will serve as the base for a larger project in which the data will be evaluated. These evaluated data will then serve as the basis for the development of a definitive set of group additivity values for implementation of Benson's Group Additivity method of estimating thermochemical data. It is anticipated that the project, to be organized and initiated during FY92, will be carried out in collaboration with teams from several other laboratories interested in the estimation of thermochemical data.

This laboratory has considerable background and expertise in this area. For example, a paper on the Benson-type estimation of the thermodynamic properties of organic oxygen- and organic nitrogen-containing compounds at 298.15 K is currently being prepared, and a companion paper on the estimation of thermodynamic properties of organic sulfur and organic halogen compounds at 298.15 K will be submitted during FY92. Also, as described above under the Chemical Database Development heading, sophisticated software for handling such estimations is already available in Division Data Centers.

Other on-going work involves data on the heat capacities of organic compounds. During the year, data from earlier compilations were merged and put into an electronic database. With this as a starting point, work has been initiated to collect and evaluate the literature which reports experimental results on heat capacities, entropies, and phase transitions of organic compounds in the condensed phase. The coverage of the literature search will include calendar years 1990, 1991, and any papers which were inadvertently omitted from either of the previous two publications. This work ties in with the current international collaboration on the IUPAC Project on the Critical Evaluation of the Heat Capacities of Organic Liquids.

The estimation of the heat capacities of various classes of liquid organic compounds using the second order group contribution approach as a function of temperature is also on-going. Polynomial expressions are being developed to accommodate group values over as wide a range of temperatures as is possible.

C. Outputs and Interactions (Chemical Kinetics and Thermodynamics Division)

1. Publications

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2. Talks

Braun, W., "UV & Vacuum UV Absorption Spectra of Small Unsaturated Molecules Pertinent to Planetary Atmospheres," Second International Conference on Laboratory Research for Planetary Atmospheres, Charlottesville, VA, October 1990.

Buckley, T.J., "Stratospheric Ozone Depletion," Temple University, Philadelphia, PA, April 1990.

Domalski, E.S., "Comparison and Test Results of Two Computer Estimation Programs and Databases," DIPPR Meeting (held concurrently with the 1990 Annual AICHE Meeting), Chicago, IL, November 1990.

Domalski, E.S., "Enthalpies of Combustion of Glycylglycine and DL-Alanylalanine," Forty-sixth Annual Calorimetry Conference, Northern Illinois University, KeKalb, IL, July 1991.

Fahr, A., "A Laboratory Investigation of the Reactions of Vinyl Radicals Pertinent to Planetary Atmospheres," Second International Conference on Laboratory Research for Planetary Atmospheres, Charlottesville, VA, October 1990.

Hampson, R.F., "Status of Rate Data for Atmospheric Reactions of Halogen Species," Meeting of IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, Montreux, Switzerland, May 1991.

Hampson, R.F., "Status of Rate Data for Atmospheric Reactions of Halogen Species," Meeting of NASA Panel for Data Evaluation, Rosslyn, VA, September 1991.

Herron, J.T., "Data Resources for Modeling Plasma Processes," Panel on Plasma Processing of Materials - Workshop, Irvine, CA, February 1991.

Herron, J.T., "Development of Data Bases at NIST for Use on Personal Computers," Workshop on Databases in Chemical Kinetics, Novosibirsk, USSR, April 1991.

Herron, J.T., "Directions for IUPAC Programs in the Chemical Kinetics Commission," IUPAC General Assembly, Hamburg, August 1991.

Hudgens, J.W., "The Discovery and Characterization of Higher Electronic States of Transient Free Radicals with Multiphoton Ionization Spectroscopy" Harvard University, Cambridge, MA, March 1991.

Hudgens, J.W., "Electronic States of Silicon Containing Free Radicals Observed by Resonance Enhanced Multiphoton Ionization Spectroscopy," Symposium on Silicon Hydrides Chemistry and Silicon CVD Mechanisms, American Chemical Society Meeting, Atlanta, GA, April 1991.

Hudgens, J.W., "Multiphoton Ionization Spectroscopy of Free Radicals Important to Surface and Combustion Chemistry," 21st International Conference on Free Radicals, Williams College, MA, August 1991.

Hudgens, J.W., "2+1 Resonance-Enhanced Multiphoton Ionization Spectroscopy of the Difluoromethyl Radical," Quantum Electronics and Laser Science Conference (QELS), American Physical Society and Optical Society of America, Baltimore, MD, May 1991.

Hudgens, J.W., "Multiphoton Ionization Spectroscopy of Difluoromethyl Radicals," 46th Symposium on Molecular Spectroscopy, Columbus, OH, June 1991.

Hudgens, J.W., "Multiphoton Ionization Spectroscopy and *ab initio* Calculations of CCl_3 and CHF_2 Radicals," 21st International Conference on Free Radicals, Williams College, MA, August 1991.

Huie, R.E., "Temperature and Solvent Dependence of the Kinetics of the Reactions of Small Free Radicals," Indian Institute of Technology, Madras, India, September 1991.

Huie, R.E., "Temperature and Solvent Dependence of the Kinetics of the Reactions of Small Free Radicals," Department of Energy, University of Madras, Madras, India, September 1991.

Huie, R.E., "The Temperature Dependence of Free Radical Reactions in Solutions," Miller Conference 91, Giens, France, September 1991.

Johnson, R.D., III, "SiH_3 Electronic States Observed by 2 + 1 and 3 + 1 Resonance- Enhanced Multiphoton Ionization Spectroscopy," Quantum Electronics and Laser Science Conference (QELS), American Physical Society and Optical Society of America, Baltimore, MD, May 1991.

Johnson, R.D., III, "Excited Electronic States of the Tropyl (cyclo-C_7H_7) Radical observed by Resonance Enhanced Multiphoton Ionization Spectroscopy," Quantum Electronics and Laser Science Conference (QELS) American Physical Society and Optical Society of America, Baltimore, MD, May 1991.

Johnson, R.D., III, "Tropyl (cycloC_7H_7) Radical Electronic States Observed by Resonance Enhanced Multiphoton Ionization Spectroscopy," 46th Symposium on Molecular Spectroscopy, Columbus, OH, June 1991.

Johnson, R.D., III, "Electronic States of the CCl Radical and Tropyl (Cyclo-C_7H_7) Radical Observed by Resonance Enhanced Multiphoton Ionization Spectroscopy," 21st International Conference on Free Radicals, Williams College, MA, August 1991.

Kirklin, D.R., "Experimental Heats of Formation of Fullerenes," Workshop on Fullerites and Solid States Derivatives, Philadelphia, PA, August 1991.

Kirklin, D.R., "Estimation Methods and Combustion Calorimetry of Organic Phosphorus Compounds," 18th Annual National Conference of the National Organization for the Professional Advancement of Black Chemist and Chemical Engineers, Washington, DC, April 1991.

Kurylo, M.J., "Current Measurements and Predictions of Stratospheric Ozone," The World Bank Seminar Program on the Ozone Layer, Washington, DC, January 1990.

Kurylo, M.J., "The Network for the Detection of Stratospheric Change: Current Progress in Ground-Based Instrumentation for Global Monitoring," Optical Society of America Conference on Optical Remote Sensing of the Atmosphere, Lake Tahoe, CA, February 1990.

Kurylo, M.J., "The Chemistry of Stratospheric Ozone: Its Response to Natural and Anthropogenic Influences," Physical Chemistry/Chemical Physics Seminar Program, University of Maryland, College Park, MD, February 1990.

Kurylo, M.J., "Stratospheric Ozone Depletion: The Impact of Recent Studies in the International Negotiation Process," IBM International Environmental Conference, Washington, DC, May 1990.

Kurylo, M.J., "The Science of Ozone Depletion," HazMat International '90 Conference, Atlantic City, NJ, June 1990.

Kurylo, M.J., "A Summary of Atmospheric Measurement Activities under NASA's Atmospheric Chemistry Programs," 1990 Johnson Conference ("Our Changing Atmosphere: Challenges in Measurement Technology"), Johnson, VT, July 1990.

Kurylo, M.J., "Recent Advances in the Study of Stratospheric Ozone," Miter Corporation Science Symposium, Fairfax, VA, July 1990.

Kurylo, M.J., "Stratospheric Ozone 1990: The Atmospheric Chemistry of CFCs and Potential Alternatives," American Chemical Society, National Meeting, Washington, DC, August 1990.

Kurylo, M.J., "Latest Developments in the Assessment of Stratospheric Ozone Depletion," Workshop on the Modeling and Chemistry of the Ozone Layer, Leningrad, USSR, September 1990.

Kurylo, M.J., "An Overview of U.S. Laboratory Research in Homogenous and Heterogenous Chemical Kinetics," Workshop on the Modeling and Chemistry of the Ozone Layer, Leningrad, USSR, September 1990.

Kurylo, M.J., "Future U.S. Plans for Polar Stratospheric Studies in the Arctic and Antarctic," Workshop on the Modeling and Chemistry of the Ozone Layer, Leningrad, USSR, September 1990.

Kurylo, M.J., "International Efforts in the Study of Stratospheric Ozone Depletion: A 1990 Status Report," 3rd Italian National Workshop on the Antarctic Atmosphere, Porano, Italy, October 1990.

Kurylo, M.J. "The Atmospheric Importance of Methyl Bromide," Briefing of the Chemical Manufacturer's Association Panel on Methyl Bromide, CMA Headquarters, Washington, DC, February 1991.

Kurylo, M.J., "The Network for the Detection of Stratospheric Change: Its Complementary Role for Satellite Programs in the 1990's and Beyond," Briefing of the Atmosphere Panel of NASA's Earth Observing System, NASA Goddard Space Flight Center, Greenbelt, MD, February 1991.

Kurylo, M.J., "The Atmospheric Characteristics of HCFC-32," EPA Workshop on R-32 and R-32 Mixtures, Washington, DC, March 1991.

Kurylo, M.J., "Present State of Chemical Knowledge of the Upper Atmosphere," NIST Chemical Science and Technology Laboratory Colloquium, Gaithersburg, MD, July 1991.

Mallard, W.G., "Logic and Implementation in the NIST Chemical Kinetics Database," Workshop on Databases in Chemical Kinetics, Novosibirsk, USSR, April 1991.

Martinez, R.I., "Instrument-Independent Database for Collisionally-Activated Dissociation in RF-Only Quadrupoles: The Acetone Molecular Cation," Twelfth East Coast ICR and Ion Molecule Chemistry Symposium, Newark, DE, October 1990.

Martinez, R.I., "Kinetics and Mechanism of the Collisionally-Activated Dissociation of the Acetone Cation," 1st Gordon Research Conference on Structures, Energetics, and Reaction Dynamics of Gaseous Ions, Ventura, CA, March 1991.

Martinez, R.I., "Kinetics and Mechanism of the Collisionally-Activated Dissociation of the Acetone Cation," 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 1991.

Martinez, R.I., "Standard Reference Spectra for MS/MS Quality Assurance, Performance Evaluation, and Proficiency Testing: X(rf)Q Tandem Mass Spectrometers," 7th Annual Waste and Quality Assurance Symposium, Washington, DC, July 1991.

Neta, P., "Electron Transfer Reactions of Metalloporphyrins. Effect of Structure and Medium on Site of Reaction in Nickel and Chromium Porphyrins," 15th DOE Solar Photochemistry Research Conference, Snowmass, CO, June 1991.

Neta, P., "Temperature Dependence of the Rate Constants for Radical Reactions," 9th International Congress of Radiation Research, Toronto, Canada, July 1991.

O'Hare, P.A.G., "Fluorine as an Oxidant in Combustion Calorimetry," Seminar, Vrije Universiteit, Amsterdam, The Netherlands, August 1991.

Stein, S.E., "The NIST Mass Spectral Database," American Society for Mass Spectrometry, Short Course on Mass Spectral Interpretation, Nashville, May 1991.

Stein, S.E., "The NIST Mass Spectral Database Program," Washington Area Mass Spectrometry Group, Short Course on Mass Spectral Interpretation, Rockville, MD, April 1991.

Stein, S.E., "The NIST Mass Spectral Database Program," HP Group Users Group Meeting, Rockville, MD, September 1991.

Stein, S.E. "The NIST Structures and Properties Database System," National ACS Meeting, NY, August 1991.

Stein, S.E., "The NIST/EPA Mass Spectral and Infrared Database Program," - EPA Conference on Air Quality Measurements - Research Triangle Park, NC, June 1991.

Stein, S.E., "The NIST/EPA Mass Spectral Database Program," EPA OSWER Conference, San Diego, CA, March 1991.

Tsang, W., "Combustion Kinetics of Hazardous Waste Incineration," Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, October 1990.

Tsang, W., "Fundamental Aspects of Hazardous Waste Combustion," SERI Workshop on the Applications of Solar Photons, Solar Energy Research Institute, Denver, CO, November 1990.

Tsang, W., "Chemical Kinetics of Hazardous Waste Incineration," Dept. of Chemistry, George Washington University, Washington, DC, December 1990.

Tsang, W., "Fundamental Aspects of Hazardous Waste Incineration," Eastern States Section of the Combustion Institute, Orlando, FL, December 1990.

Tsang, W., "What We Don't Know About Unimolecular Reactions," Washington Area Photochemistry Group, Catholic University, Washington, DC, February 1991.

Tsang, W., "Data Base for Combustion Chemistry," Workshop on Databases in Chemical Kinetics, Novosibirsk, USSR, April 1991.

Tsang, W., "Fundamental Aspects of Hydrocarbon Pyrolysis," Wright-Patterson Air Force Base, OH, May 1991.

Tsang, W., "Problems in the Incineration of Hazardous Wastes," Dept. of Chemistry Cornell University, Ithaca, NY, July 1991.

Tsang, W., "The Incineration of Perchloroethylene and Chlorobenzene," AICHE Winter Meeting, Chicago, IL, November 1990.

Tsang, W., "The Pyrolysis of 1,7-Octadiyne as a Source of Propargyl Radicals," ACS National Meeting, New York, NY, August 1991.

3. Committee Assignments

K.C. Churney
- ASTM E-37 Committee on Thermal Analysis
- U.S. Calorimetry Conference
- ASTM E-27 Committee on Hazard Potential for Chemicals

E.S. Domalski
- U.S. Calorimetry Conference (Counselor and Member)
- ASME Research Committee on Industrial and Municipal Waste (Assoc. Member)
- IUPAC Commission 12 Subcommittee on Thermodynamic Data (Secretary)
- ASTM E-27 Committee on Hazard Potential for Chemicals, Subcomittee E27.07 on Estimation Methods

R.F. Hampson
- NASA Panel for Data Evaluation
- IUPAC Commission on Chemical Kinetics, Subcommittee on Gas Kinetics Data Evaluation for Atmospheric Chemistry (Secretary)

J.T. Herron
- Organizing Committee, International Conference on Chemical Kinetics (Chairman)
- IUPAC Commission on Chemical Kinetics (Chairman)
- IUPAC Subcommittee on Data for Low Pressure Plasma Chemistry
- JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry

R.E. Huie
- Poster Session Committee, CHEMRAWN VII
- Environmental Protection Agency Grant Review Panel
- American Working Group in Physical and Material Sciences of the Indo-US Subcommission on Science and Technology

J.W. Hudgens
- University Research Instrumentation Program Review Panel for Capital Equipment Grants
- NIST Chemical Science and Technology Laboratory Colloquium Committee

D.R. Kirklin
- U.S. Calorimetry Conference
- National Organization for the Professional Advancement of Black Chemists and Chemical Engineers
- ASTM E-34 Committee on Waste Management

M.J. Kurylo

NASA Panel for Data Evaluation

Network for the Detection of Stratospheric Change, Chairman of Steering Committee

S.G. Lias

ASTM E-49 Committee on Computerization of Material Property Data

Joint Committee on Atomic and Molecular Physical Data

American Society for Mass Spectrometry Measurements and Standards Committee

R.I. Martinez

Washington Editorial Review Board

Experimental Hazards Committee

D. Neumann

ASME Research Committee on the Properties of Water and Steam

P.A.G. O'Hare

U.S. Calorimetry Conference

Scientific Organizing Committee, IUPAC Conference on Chemical Thermodynamics, Snowbird, UT 1992

IUPAC Commission on Thermodynamics (Titular Member, Chairman)

L.W. Sieck

Panel for Small Business Innovative Research Program of the U.S. Department of Energy

S.E. Stein

Air Pollution Modeling Instrumentation and Measurement Methodology Group

Review Committee, 23rd International Symposium on Combustion

W. Tsang

JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry

Review Committee, 23rd International Symposium on Combustion

4. Others

a. Editorships

M.J. Kurylo

International Journal of Chemical Kinetics (Editorial Board)

S.G. Lias

Journal of Physical and Chemical Reference Data (Editorial Board)
Molecular Structure and Energetics, VCH Publishers, Inc. (Editorial Board)

R.I. Martinez

NIST Journal of Research (Editorial Board)

P. Neta

Radiation Physics and Chemistry (Regional Editor)

P.A.G. O'Hare

The Journal of Chemical Thermodynamics (Editor)

S.E. Stein

ACS Chemputer Guide (Editorial Board)

b. Seminars

March 20, 1991

V.M. Zamanskii, Institute of Chemical Physics, Moscow, USSR, "Promotion of High Temperature Chemical Reactions." (Division Sponsor: W. Tsang)

April 16, 1991

Konstantin Lebedev, Boris Derendyaev, and Vaddim Piottukh-Peletsky, Institute of Organic Chemistry, Novosibirsk, USSR, "Computer-Assisted Determination of Molecular Structure from Analytical Spectra." (Division Sponsor: S.E. Stein)

April 16, 1991

Jean Futrell, University of Delaware, Newark, Delaware, "Fundamental Mechanisms of Collisionally Activited Mass Spectrometry." (Division Sponsor: R.I. Martinez)

May 24, 1991

Michael J. Pilling, University of Leeds, Leeds, U.K., "Elementary Reactions and Combustion Processes." (Division Sponsor: J.T. Herron)

July 16, 1991

Elwin C. Penski, U.S. Dept. of the Army, Aberdeen Proving Ground, Maryland, "Estimation and Statistical Treatment of Physical and Thermodynamics Properties of Organic Liquids." (Division Sponsor: E.S. Domalski)

September 6, 1991

Simon G. Clement, University of Bristol, Bristol, U.K., "Multiphoton Ionization Studies of the NH Radical." (Division Sponsor: J.W. Hudgens)

c. SRM Activities

39j Benzoic Acid (recertification)
2231 Indium
2682a Sulfur in Coal
2685a Sulfur in Coal

d. SRD Activities

1, NIST/EPA/MSDC Mass Spectral Database, Update
17, Chemical Kinetics, Update
18, THERM/EST, Update
25, Structures and Properties, New
DIPPR Project 861, Aqueous Electrolyte Solution Database, New

INORGANIC ANALYTICAL
RESEARCH

IV. Inorganic Analytical Research Division (834)

James R. DeVoe, Chief

A. Division Overview

The Inorganic Analytical Research Division conducts research and development on the accurate quantitative measurement of the chemical composition of materials. The effectiveness of our program is continually tested via the Standard Reference Materials (SRM) program; our measurements on these materials are constantly being intercompared both within and outside of NIST. We have several strong programs in the Division: in nuclear methods of analysis because these measurements are based upon physico-chemical principles that are different than most others and thereby provide a unique approach to accuracy; in mass spectrometric methods because they provide measurements of high precision and accuracy; in optical methods because of their predominant use in most analytical laboratories; and in electrochemical methods because of the critical needs for standards in pH and conductance.

Collaborations with scientists in industry and universities continue, with the number of guest scientists working in our laboratory from industry, universities, and other government agencies currently at 33. In addition, we continue to perform a number of non-routine chemical analyses for other organizations. In most cases, these analyses are for the purpose of establishing a benchmark measurement for a specific type of material of interest to industry or other government agencies.

The following paragraphs provide a Divisional perspective of selected accomplishments over this past year for each of the groups. Some of these projects are elaborated upon in the highlights to follow.

The potential for high-accuracy mass spectrometric measurements rests in the high precision with which isotope abundance ratios can be measured. This precision ranges from a few parts in 10^5 when using thermal ionization with E/M focussing (TIMS) to a few parts in 10^3 when using an inductively coupled plasma source with quadruple focussing (ICP-MS). The use of ICP-MS is gaining importance because our experience over the past three years in evaluating its performance and in improving various parts of the system have shown it to be suitable for the certification of Standard Reference Materials (SRMs) at somewhat lower costs than TIMS. This past year slightly more than half of the approximately 60 elemental determinations in fourteen SRMs performed by mass spectrometry were done by ICP-MS.

Assay and purification procedures have recently been developed and verified in preparation for the determination of the atomic weight of zinc. The atomic weight of zinc determination is one of the least well-known in the periodic table; this research project should improve its accuracy by a factor of ten. This will be the 17th element for which the atomic weight has been determined at NIST. In addition to the importance of having accurately known atomic weights, this project provides the opportunity to develop and perfect the necessary expertise for the certification of SRMs by isotope dilution. The next step for the atomic weight of zinc is to develop and evaluate the mass spectrometric procedures.

The measurement of the isotopic ratios of boron was studied in collaboration with Prof. William Leeman (Guest Scientist) of Rice University. A method was developed suitable for the certification of SRMs. In addition, these studies have significantly improved the sensitivity for measuring isotopic fractionation effects that are used by geologists as indicators for geochemical and geophysical processes. To perform isotope dilution mass spectrometry with accuracy consistent with the instrumental precision, meticulous chemical separations need to be performed. Such separations are time consuming, particularly if conventional methods of chemical separation are used. Chromatographic methods are often ideally suited for this application. Furthermore, the procedures can be automated, thereby eliminating some of the tedium of hand-operated separations. Current studies involve the separation of the rare earths. Extension of these methods to other elements will be attempted in the future.

The effort to improve the various electronic components in mass spectrometers continues, while de-emphasizing the design and fabrication of complete mass spectrometers. Such improvements result in increasing the precision and accuracy of isotope ratio measurements. This past year a teslameter (gaussmeter) was designed. The stability and resolution of this instrument significantly surpasses any commercial unit. Over this next year a number of the NIST mass spectrometers will be fitted with these instruments.

A series of SRMs for aqueous electrolytic conductivity has been completed. In addition, a recommendation was submitted to, and accepted by, the International Union of Pure and Applied Chemistry (IUPAC) for electrolyte conductivity standards based upon the molal concentration scale. A new conductivity cell has been designed and tested, and will be used for certification of the renewal SRMs next year. In addition, conductimetric procedures developed this year for evaluating the dissociation constants for amino acids will be further evaluated to determine the extent of applicability of this technique.

Several important pH studies have been completed. A detailed mechanism of the response of the glass electrode to pH has been elucidated. The pH of the MOPSO buffer system has been studied in preparation for the certification of an SRM as reported below. In addition, considerable effort has been given to working with other organizations in the establishment of pH standards. We have intercompared pH buffer standards with Radiometer A/S, which is the Danish national standards laboratory in this field. We also have worked with American Society for Testing and Materials (ASTM) on establishing consensus standards for the pH of rainwater and with the National Committee for Clinical Laboratory Standards (NCCLS) on sodium and potassium in blood serum.

Highly accurate, controlled-current coulometry for the absolute assay of high-purity chemicals as SRMs has been greatly improved this year through the development of an automated system, as reported below. The newly demonstrated automated coulometric titration system removes the tedium of this absolute analytical method and also is expected to improve the precision by minimizing the component of random error due to operator intervention.

Heavy emphasis has been placed this past year on the certification of SRMs by optical methods. Over 15 elements in each of more than 60 candidate materials were certified. Most notable among these are the spectrometric solutions, which are used to calibrate instrumental methods. Special attention was devoted to the stoichiometry and purity of the compounds that have been used as the starting materials for these solutions. Emphasis next year will be on a series of lead SRMs, including a lead paint film for calibrating portable X-ray fluorescence instruments, and lead in old paint and soils. The large demand by industry for transmittance filter standards is making it necessary to design and assemble a second instrument to assume part of the workload associated with making the calibration measurements. The use of slurried samples in graphite furnace atomic absorption spectrometry was applied to the evaluation of homogeneity of select elements in several reference materials. X-ray fluorescence was transferred to this Division and will be used extensively to determine homogeneity of elemental constituents in prospective SRMs.

Optical methods have been used to characterize high-temperature superconductors. Data on impurity concentrations and the stoichiometry of the compounds were obtained using inductively coupled optical emission spectrometry (ICP-OES). Stoichiometry could be verified to within a few parts per thousand, an accuracy comparable to that usually preserved for classical wet chemical methods of analyses.

After two years of study, the Fourier transform UV/VIS spectrometer is operational. This instrument is currently being used in two areas. A collaboration with Iowa State University is under way to generate ICP-OES reference spectra of the elements. The FT will be used to provide high-accuracy wavelength calibration. In addition, the instrument is being used to generate high accuracy reference spectra for the purpose of generating a library that can be used with various mathematical algorithms to resolve complex optical emission spectra into their components. Future studies will be made on the distribution of noise in the spectra with the possibility of using the spectral information for quantitative analysis.

The analytical uses of laser spectroscopy have always suffered from a lack of low-cost, reliable, easy-to-use lasers. Recent developments in tunable diode lasers have shown promise in fulfilling these requirements. Studies on the use of these lasers in fluorescence and ionization have been initiated.

The application of wet chemical methods of analysis continues to expand and improve, especially in the determinations of major components of SRMs. This past year was highlighted by an article in Analytical Chemistry which reminded the readers of the importance of wet chemistry and its role in contemporary analytical chemistry.

The use of a variety of nuclear methods has continued to contribute to the certification of SRMs, determining over ten elements in ten materials this year. Our core capability for certifying SRMs by nuclear methods has been substantially improved by the replacement of part of the professional staff lost during the previous year.

A systematic error in prompt gamma activation analysis (PGAA) was observed in which element sensitivities (cps/mg) increased with increasing hydrogen concentration. The process responsible for this enhancement is neutron scattering. Monte Carlo calculations demonstrated that, depending on the absorption and scattering properties of the sample (which include sample size, shape and orientation with respect to the neutron beam), significant errors can affect the accuracy of the method. Theoretical calculations have shown that for spherical samples these errors are minimized. Experimental PGAA measurements on spheres have confirmed this theory; thus for samples containing significant levels of hydrogen, special sample preparation will be necessary.

Considerable effort has been expended on the analytical applications of cold neutrons. State-of-the-art instruments for both PGAA and neutron depth profiling (NDP) have been designed and constructed. For NDP, a new, highly versatile 60-cm diameter chamber has been designed for ultra-high vacuum capability. The final configuration allows remote computer-controlled scanning of samples and rotation of both sample and detector angles relative to the beam. In collaboration with the Eastman Kodak Company, depth profiles have been made on a cobalt nickel oxide produced with enriched $^{17}O_2$ for the first time.

A permanent, full-time instrument for PGAA has been constructed as part of the Cold Neutron Research Facility. This new facility will allow accurate measurements of low levels of a number of elements, including hydrogen. Hydrogen detectability to a few tens of micrograms has already been achieved. This promises to be of value in numerous applications where quantitative, nondestructive determinations of small quantities of hydrogen in materials are necessary. Further background reduction by one to two orders of magnitude is probable in the near future. This will permit the resolution of a discrepancy in the current measurement technology for hydrogen in metals. Currently, measurements made in the U.S. and Europe using gaseous effusion do not agree; this PGAA technique which uses a different approach may resolve the problem.

In conjunction with a long-range program to explore and develop the analytical applications of focused beams of cold neutrons, we have demonstrated the ability to focus neutrons for the first time. Our goal is to produce beams of neutrons with intensities several orders of magnitude greater than previously available. Such beams will greatly enhance the capabilities of both PGAA and NDP and may ultimately lead to a neutron probe for microanalysis.

The Consortium on Automated Analytical Laboratory Systems was established two years ago to develop new methods of automating chemical analysis and to standardize communication between instrument system components thereby facilitating the assembly of a complex analysis system from component parts. One project in inorganic analysis involves the use of microwave heating for chemical dissolution, and another project in organic analysis, conducted in the Organic Analytical Research Division, involves the study of supercritical fluid methods for extracting components from environmental samples. A modularity project involves the definition of building blocks that make up a total chemical analysis system, and the definition of protocols for communicating between the modules.

For the inorganic project, an automated microwave dissolving station has been constructed for handling environmental samples. This next year we plan to interface this station through a flow-injection analyzer to an ICP-OES instrument. For the organic project a study has been completed on the supercritical fluid extraction (SFE) of diesel fuel from clay matrices, and a publication is in process.

B. Selected Technical Reports (Inorganic Analytical Research Division)

1. CAALS at Two Years: A Progress Report

G.W. Kramer

The Consortium on Automated Analytical Laboratory Systems (CAALS) is an interactive organization with membership from U.S. industries and other government agencies. Its purpose is to promote the advancement of automated analytical systems, to improve laboratory efficiency and data quality, and to promote transferability of analytical methods so that U.S.-based industries realize competitive advantages in chemical measurement technology. CAALS areas of competence include: laboratory automation, instrumentation development, laboratory robotics, automated analytical chemical methods development, microwave sample preparation, and automation of chemical separations methods. Now in its second year, the Consortium has grown from the proposal and formulation stage, through development and acceptance, to active participation by over ten industrial firms and other government agencies.

The CAALS Oversight Board (OSB) has met twice this past year to review projects, set directions, and discuss priorities in laboratory automation. Participation in OSB meetings, which has been active and spirited, demonstrates the interest and importance that industry places on laboratory automation. The Oversight Board has approved three projects: the Modularity and Control Communications Standards Project—a program to develop modular instruments and to standardize inter-instrument communications, an organic analysis effort to formulate new automated methods for the preparation and extraction of organic analytes, and an inorganic project to create a totally automated system for the analysis of trace metals.

The Modularity and Control Communications Standards Project addresses the problems of instrument connectivity and interoperability in analytical chemistry. The goal is to establish interfacing standards to make it easier to interconnect individual instruments into complete analytical systems. CAALS has proposed that instruments or aggregates of instruments be created as modules whose interactions with the external world must be specified in the areas of sample interchange, data interchange, and control/status interchange. CAALS is developing, primarily through workshops held quarterly at NIST with technical representatives from member organizations, guidelines for creating modular instruments which can be used to build analytical systems.

The Organic Analysis Project (in collaboration with the Organic Analytical Research Division) is examining new methods for extracting organic analytes from environmental sample matrices. Chief among these is supercritical fluid extraction (SFE), where supercritical carbon dioxide with small amounts of liquid solvent additives is used as the extraction medium. The CAALS efforts are specifically directed at the quantitative aspects of the extractions. The hope is that SFE, using its non-toxic extraction fluid, can be used to replace traditional Soxhlet and sonication methods.

The Inorganic Analysis Project involves creating the first example of a totally automated, modular analytical system for the determination of trace metals in environmental samples. Consisting of three separate modules, this project also provides a test bed for demonstrating and evaluating CAALS modularity and instrument interfacing concepts. In the first module, samples are prepared for analysis using microwave-assisted acid dissolution or leaching procedures. Dissolved analytes will be processed through a separation/clean up module built around a flow-injection system and then connected to an elemental detection and quantitation module (ICP-OES).

2. Determination of Rare Earth Elements in Coal Fly Ash by Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry

D.S. Braverman

The determination of rare earth elements (REE) by mass spectrometry has traditionally been difficult and time-intensive, requiring both chemical separations and multiple mass spectrometric runs. The problems result from the similar chemical properties of the REE and the fact that the oxides of the lighter REE tend to interfere with determination of the heavier REE. To overcome these problems, a new procedure has been developed that combines liquid chromatography (LC) and inductively coupled plasma mass spectrometry (ICP-MS). The direct coupling of the LC with the ICP-MS results in relatively fast REE measurement with minimal elemental overlap and minimal isobaric interferences. Coal fly ash was analyzed to evaluate the procedure.

A LC system that can function in both isocratic and gradient modes of operation was assembled. A gradient separation procedure was developed that completely separated 12 of the 14 REE in under 40 minutes. However, complete separation of the REE is not required since the mass separation of the ICP-MS provides complementary capabilities to the LC. Thus, an isocratic separation was developed that proved more than adequate. The heavy REE elute as a group early in the chromatogram, while the remaining elements elute singly or in pairs. Barium, whose oxide can also interfere, elutes after all the REE. This isocratic separation is time efficient, and it resolves both the oxide interferences and other isobaric interferences such as the one between ^{142}Ce and ^{142}Nd.

Isotope dilution was done to provide accurate concentration measurements. Two specific problems were avoided using this technique. First, the ICP-MS has significant signal drift over the course of a day. Since the time delay between chromatograms is relatively long, an external standard approach is not feasible until the long term stability of the instrument improves. Second, a preliminary clean-up of samples is necessary to avoid problems with column clogging. In this work, an open column separation was employed to separate the REE as a group from most other elements. Direct ICP-MS analysis of preliminary fly ash samples indicated the partial loss of some heavy rare earth elements (Dy, Ho, Er, Tm, Yb, and Lu) during this clean-up. Losses ranged from a high of 14% for Yb to 0.5% for Dy. Complete recoveries are not required when doing isotope dilution analysis, since it is the isotopic ratio which determines the concentration in the original sample.

The ICP-MS detection limits were in the sub-nanogram region. Sensitivity was not a problem with the coal fly ash samples. In fact, it was necessary to dilute the samples to avoid saturation of the detector during measurement. The measured values for the eight REEs quantified agreed well with literature values. Three separate aliquots were injected onto the column for each sample. The measured precision for sample injection averaged 6%. In some cases, more than one ratio pair was measured for an element and good agreement between pairs was observed. A detailed statistical analysis was performed on the data to determine the variance components. This analysis indicated that the error associated with each isotope ratio pair is predominantly due to measurement error rather than sample preparation. Uncertainty due to counting statistics ranged from 0.3% for Ce to a high of 1.6% for Eu.

Further work is under way to compare these results and those obtained using LC coupled with ultraviolet detection after post column derivatization. The accuracy of isotope ratio measurement will be evaluated by off-line LC separation followed by thermal ionization mass spectrometry. Further LC-ICP-MS studies are needed to trace the sources of measurement imprecision.

3. The Development of the NIST Teslameter, The Final Phase

R.W. Shideler

Magnetic sector mass spectrometers rely on precisely established, tightly controlled magnetic fields. The control units used on the NIST machines are obsolete and there are no adequate instruments on the market today for magnetic field measurement and control. The typical Hall device unit has a resolution of 4 digits or fewer and lacks stability for this application. NMR type instruments have the resolution but are expensive, are difficult to operate, and have large, clumsy probes. The units now being used cannot provide the improved accuracy or the other features necessary to follow promising new lines of research.

To address this growing concern, a new controller has been designed and the first prototype instrument has been successfully completed. The NIST Teslameter project has now entered into its final phase.

A series of operational tests were performed using the mass spectrometer designated NIST Number 1. In all important aspects, the performance of the NIST Teslameter showed significant operational benefits. One area of improvement was the seek time of the control circuit which settles on a new value in tenths of seconds. The initial problem of having a thermal gradient along the length of the probe was rectified by putting the load resistor close to the Hall element so that there was no temperature gradient possible between the two parts. A second prototype unit was constructed at this time and is in service at the laboratory of Professor Gil Hanson at SUNY Stony Brook. The instrument has performed well.

While each of these two instruments are operating satisfactorily, certain operational deficiencies have surfaced during the testing phase. The most crucial of these has to do with the limited resolution (1-part-in-256) of the temperature compensation analog-to-digital converter (ADC). The redesign of two of the boards was undertaken. The digital board holding the offending 8-bit ADC was upgraded to 12 bits, providing a resolution of 1-part-in-4096. The analog board was redesigned to take advantage of an improved layout and to implement many minor circuit changes. A new board, the "mother board," was included which would make possible more expedient construction as well as provide improved stability. Other necessary refinements to the design include:

- Addition of a bit in the composite digital-to-analog converter (DAC) giving it 20 bits resolution.
- Stabilization of the metering resistor thermal compensation to remove residual fluctuations due to temperature cycling.
- Addition of a true drive current constant source generator to improve reference stability.
- Replacement of the small-scale logic of the digital control board with a programmable array logic device (PAL), thereby relieving congestion on the board and providing more reliable operation.

Other improvements in the design were made as well. A Hall probe, thin enough to slip between the flight tube and the magnet pole face, is being fabricated. The sensitive region of the Hall device is placed long the ion flight trajectory in the magnet gap which reduces the control of the field to a problem in two dimensions instead of three. This high quality Hall device, with its calibration data, will permit accuracies better than 0.1%, thereby, ending the necessity for routine calibrations that interrupt the mass spectrometric measurements. The improvement in settability provides an instrument with a resolution of 1 part in 10^6 which is real, repeatable, and monotonic, with a calibration accuracy capable of finding any mass peak. The unique AC bridge design renders this instrument free of the long term drifts often associated with other Hall device meters, and thus it stands alone in the field of Hall-device controllers. The construction of two units of the revised design is now at the point of final assembly, and electronic testing is imminent.

4. The Accurate Analysis of Lead in Blood and Other Materials - Standards and Methods Development

R.D. Vocke, K.E. Murphy, and P.J. Paulsen

Lead poisoning has been recognized as the nation's No. 1 environmental threat to children - whether they live in inner-city public housing or immaculate suburban homes. In October of 1991, The Health & Human Services' Centers for Disease Control set a "threshold for concern" for lead in blood at 10 µg/dL (≈100 ppb Pb) and required the screening of young children for elevated blood lead levels. Various estimates suggest that over 3.5 million U.S. children under the age of six may be above this new action level, and therefore are at risk. Given the scope and potential economic impact of these new requirements, it is essential that these difficult measurements are of the highest quality and reliability, while remaining routine and cost effective.

Standard Reference Material programs at NIST are presently underway (Pb in Blood, Pb in Paint) to provide the accurate standards to benchmark the required Pb measurements. Isotope dilution mass spectrometry (IDMS) has been crucial in our efforts to provide values with the highest precision and accuracy. Specifically, the certification of the new Pb in Blood Standard Reference Material (SRM 955a) was done by IDMS using an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS). The relative lack of chemical processing required for ICP-MS analysis ensured that Pb blanks during analysis could be minimized. This allowed us to keep the analytical uncertainties to less than 1% (95% confidence level), even at very low Pb concentrations (<50 ppb Pb). The quality of the bovine blood prepared and bottled by CDC, together with our control on the analytical precision has resulted in a renewal SRM that has almost an order of magnitude less variability relative to the original porcine blood standard, particularly at lower Pb levels. The unique properties of IDMS have also allowed us to make accurate measurements of Pb in Paint at the percent level, even when a solid residue precipitated out of the solution subsequent to spiking and dissolution.

We are also developing a precise and accurate method for Pb determination based on a simplification of the technique of isotope dilution analysis in order to transfer an established, precise and highly accurate NIST protocol to the public and commercial sector. Traditional isotope dilution analysis requires two separate analyses to fully characterize a sample. The methodology we propose capitalizes on the low and relatively constant atomic abundance of ^{204}Pb in natural lead. A single analysis of a sample, spiked with a ^{204}Pb tracer, will yield accurate Pb concentrations, regardless of the amount of Pb in the blood and its isotopic composition. In addition, the relative abundance of the three radiogenic isotopes of lead (^{208}Pb, ^{207}Pb and ^{206}Pb) can also be determined. Because these isotopes vary considerably in nature, the isotopic composition of lead can often be used to identify sources of lead poisoning. Thus, a mass spectrometric method with a ^{204}Pb spike would provide not only the concentration of Pb in blood, but would also provide additional information not available from non-mass spectrometric analytical methods. By reducing the quantitative steps during sample handling, this IDMS approach should lead to increased reliability and robustness, making it ideal for automation, and thus suited to the needs for sensitive and accurate Pb measurements into the next century.

5. Calcium Isotopic Analysis Using Laser Autoionization

X. Xiong, L.J. Moore, and J.D. Fassett

Resonance ionization mass spectrometry is a technique that combines the ability of laser radiation to photoionize gas phase atomic species selectively and efficiently with the mass resolution capabilities of mass spectrometry. In the past we have applied RIMS to both fundamental atomic spectroscopy problems and isotopic and analytical measurements. This year we have continued these applications of RIMS in collaboration with Eastern Analytical, Incorporated, with the principal element under study being calcium. The goal of the research is to develop a technique to measure calcium's role in nutrition using stable isotope tracers and to develop a screening capability for the measurement of calcium absorption.

High sensitivity measurement is emphasized in this research for several reasons. First, it is desirable to use small samples because some targeted populations, such as neonates, cannot supply large samples. Second, high sensitivity will reduce the amounts of separated stable isotopes required in these measurements, thus reducing their potentially significant cost. Third, minor isotopes of calcium (42, 43, 46, and 48) whose abundances are < 0.5% of the total calcium are typically used. Ten microliters of serum will have <5 ng of these isotopes present. Thus, the basis of spectroscopic investigations was the identification of efficient and robust schemes for calcium ionization that can be applied using evolving CW (continuous wave) laser technology. Schemes using both autoionizing resonances of Ca and wavelengths that promise to be accessible with titanium-sapphire (CW) lasers were investigated.

Autoionizing atomic levels have energies above the ionization potential of an element. Quantitative studies of several previously observed levels (3d4f, 3d7p, 3d5f) and several newly observed levels were made. Linewidths and ionization rates were studied and oscillator strengths have been estimated. These experiments were done using a thermal atom source for calcium and the pulsed lasers presently available.

A second aspect of this work was the demonstration of the fidelity of isotopic ratio measurements. A series of urine and serum samples that had their calcium isotopic values changed in a nutrition study were examined. The samples were split and reference measurements made using thermal ionization mass spectrometry. Resonant photoionization was first planned using one wavelength at 421.5 nm (2-photon transition, $4s^2$ to 3d5s) and a targeted autoionization resonance at 865 nm (3d5s to 3d7p). A more efficient autoionizing transition was observed at 861 nm, however, and isotopic measurements were made using this wavelength. The $^{44}Ca/^{42}Ca$ ratios in these samples ranged from 0.495-2.96 (natural 3.219). The average difference between TIMS and RIMS measurements was 1.3% with a standard deviation of 2.1%. These results verify the capability to make accurate isotopic measurements with our RIMS apparatus. The precision is consistent with our experience and is attributed to the variability in the pulsed ionization process.

6. Determination of Sulfur in Fossil Fuels

K.E. Murphy and W.R. Kelly

The environmental impact of burning fuels high in sulfur content has been a concern for the last two decades. The SO_2 emissions from all fossil-fueled power plants are controlled by federal and state regulations which have required power companies to monitor closely the S content of fossil fuels being used and the S emissions from the stack. Furthermore, the price of fossil fuels is determined by its S content, as well as other physical and chemical characteristics. The two common methods of S analysis used by fuel companies are X-ray fluorescence and high temperature combustion followed by infrared or iodimetric titration. These techniques are precise, cost effective, and have rapid through-put; however, both of these methods depend on external standards for calibration and can be no more accurate than the standards used.

To meet the need for accurate S standards, the Mass Spectrometry Group has developed an isotope dilution technique (ID-TIMS) for the analysis of S in Standard Reference Materials (SRMs). This procedure involves the equilibration of an enriched isotope of S (^{34}S) with the S in the sample. The sample is spiked and the sample combusted in a closed system (Carius tube) at high temperature and pressure using a mixture of HNO_3 and HCl. This treatment oxidizes all S species to sulfate. The S is then reduced to hydrogen sulfide and adsorbed into an ammoniacal solution of As^{+3}. The spike to sample ratio is determined on a thermal ionization mass spectrometer as the AsS^+ molecular ion. The technique is inherently accurate and precise because once the S spike isotope is equilibrated with the S in the sample only a measurement of the isotopic ratio of the resulting mixture is required. This ratio is not affected by chemical yields as long as the blanks are small. The amount of S in an unknown sample is quantified through knowledge of this ratio, the amount of spike added, and the sample weight.

This past year two coal and four oil SRMs were certified using the method of ID-TIMS. Three of these are particularly noteworthy because they represent recertifications of materials previously measured by this technique and serve as an example of the long-term control of the technique. For a homogeneous sample, experience has shown that the total uncertainty (random and systematic) should be about 0.3% if the blank correction is negligible. The uncertainties for the oil samples are 0.6% or better indicating good homogeneity of the samples. SRM 1622c was originally certified in 1985 and has been used twice as a control five and six years later. All three determinations are in good agreement indicating good control of the measurement process and long term stability of the SRM.

In the case of the SRM 2682 and 2685, coals, the uncertainty is above 1%. These two SRMs were reissued and recertified as 2682a and 2685a after the parent material was spin riffled to improve the homogeneity. The success of the spin riffling is indicated by the marked reduction in the uncertainty of the new S determinations, a factor of 3 and 6, respectively. The mean values of these materials are indistinguishable from those certified 8 years ago. In FY92, this technique will be applied to the determination of S in soils, sewage sludge, tomato leaves, and diesel fuel.

7. Determination of Trace Element Impurities In High Temperature Superconductor Starting Materials

D.A. Becker

In recent years, the entire field of superconductivity has been revolutionized by the discovery by Bednorz and Muller at IBM that certain types of metallic oxides become superconductive at about 35 K. Since that time, many laboratories and scientists have been investigating the mechanisms and structures of a wide variety of materials, looking for the next step towards room temperature superconductivity. Progress has been made, and useful systems which are superconductive at almost 100 K have been devised. Currently, one of the most promising is the yttrium-barium-copper-oxygen system. This system is being investigated as part of the NIST Superconductivity Program, as well as for programs in many other laboratories. As part of the NIST program, the Nuclear Methods Group was asked to provide analytical support for the materials research groups that were involved. This support involved both compositional and stoichiometry analyses of the various starting materials used in fabricating these high-temperature superconductors.

A total of 13 starting and intermediate materials were analyzed for up to 19 elements. Samples of each material weighing ~ 100 mg were encapsulated in acid cleaned polyethylene vials and heat sealed. Previously determined NAA constants normalized to iron foil fluence monitors were used as standards. Standard Reference Material 1633, Coal Fly Ash used as a control material to confirm the determined values. Samples and standards were irradiated for four hours in the NBSR RT-4 pneumatic tube irradiation facility at a reactor power of 19 MW and a neutron fluence rate of 2.7×10^{13} n cm^{-2} s^{-1}. After irradiation, samples were counted on a 15% efficient Gamma-X high purity germanium detector and associated pulse height analysis system, starting about 30 days after irradiation. The most elements actually detected in any one sample was 13, and the average number of elements detected in each sample was eight. The elements determined and the ranges of impurity concentrations found in the superconductor starting materials were as follows: ytterbium, <0.01-1.1 µg/g; selenium, <0.01-0.7 µg/g; thorium, <0.003-0.7 µg/g; chromium, <0.02-6.1 µg/g; iridium, <0.02-6.2 ng/g; hafnium, <2 ng/g; barium, <2-320 µg/g; strontium, <1-970 µg/g; cesium, <0.001-2.0 µg/g; terbium, <0.002-0.32 µg/g; scandium, <0.05-37 ng/g; rubidium, <0.2-13 µg/g; iron, <1-67 µg/g; zinc, <0.05-410 µg/g; tantalum, <3-42 ng/g; cobalt, <5-670 ng/g; silver, <0.01-2.9 µg/g; europium, <0.5-1400 ng/g; and antimony, 0.02-14 µg/g. The range of impurities in the various starting materials submitted was great. For example, four different copper oxides were analyzed, with total measured impurities ranging from 2.51 µg/g to 461 µg/g. The worst case was a yttrium-barium-copper intermediate, with almost

1300 µg/g of measured impurities. On the other hand, in some highly purified materials, the total measured impurities were below 3 µg/g.

In conclusion, INAA is a highly useful analytical technique for the measurement and evaluation of trace element impurities in many of the high temperature superconductor starting materials.

8. The Focusing of Cold Neutrons for Absorption Measurements

H. Mayer-Chen, R.G. Downing, and D.F.R. Mildner

The sensitivity of both neutron depth profiling and prompt gamma activation analysis at the NIST reactor can be substantially enhanced by the use of cold neutrons, because the absorption cross sections are much higher. In addition, these low energy neutrons have optical properties which are analogous to those of photons, and they may be focused to produce much higher fluxes using mirror reflection at small grazing incident angles. This allows much greater spatial resolution and can lead to a new microprobe which complements other radiation techniques for multidimensional analysis in materials science. We have started a series of measurements to assess the use of two different concepts to achieve the focusing of neutrons. These neutron measurements have been performed in conjunction with the development of the new charge injection device (CID) neutron detector with a 25 µm spatial resolution.

The first concept is to use a large number of nickel-coated single crystal silicon wafers as the focusing element to produce a line focus. We have studied the neutron reflection properties of the 200 µm thin wafers to be used to construct a microguide in which the neutrons are transmitted through the silicon and reflected by the nickel. A large number of these wafers, stacked and bent to a particular radius of curvature with an appropriate variation in the length, can be formed into a neutron lens to focus a large area beam onto a high-intensity line with a width in the millimeter range. These wafers have been characterized with x-ray reflectivity measurements on a synchrotron source.

The wafers are stacked and oriented along the direction of the neutron beam. The guide length formed by the wafers is 2 inches (the diameter of the wafers). The sample stage is rotated with respect to the incident beam, and those neutrons incident with an angle smaller than the critical angle of the total external reflection are reflected from the wafer surfaces. Ultimately, we wish to focus a "white" neutron beam for material research, and neutron measurements on a polychromatic beam have shown that these wafers can deflect the neutron trajectories successfully. We are undertaking more precise neutron measurements using a monochromatic beam for a better understanding of the performance of the device.

In collaboration with scientists in Grenoble, France, we have carried out cold neutron transmission measurements through the 200 µm wafers using neutrons of wavelength 7 Å. Using a well collimated incident beam, rocking curve measurements have been conducted on straight wafers placed end-to-end and side-by-side, and on curved wafers. When the straight wafers are placed end-to-end, we observe the expected broad angular response, with a width dependent on the critical angle of the silicon-nickel interface, essentially independent of the number of reflections necessary for transmission. Such measurements, some of which include up to eleven orders of reflections, show that within the entire angular range the measured reflection coefficient for the internal silicon-nickel interface has the value of 0.988± 0.005.

The second idea is to use capillary optics, a concept which has proved successful with X-rays. Technology has enabled thousands of channels to be formed within a glass fiber of sub-millimeter diameter. The transmission properties of these fibers depend critically on the design of the lens, including the glass material and its smoothness, and the internal diameter and curvature of the capillaries. Each fiber of diameter 0.2 mm has a hexagonal cross section, containing over one thousand capillaries. Each capillary has an internal diameter of 6 μm, and an external diameter of 10 μm. The lens is formed by bending and orienting the fibers in such a way that the beams emerging from each fiber point to the same small spot, and so increase the current density. In principle, the capillary lens transports neutrons in the same way as the silicon wafers, except that the capillaries can focus in two dimensions rather than one. In collaboration with scientists at the Kurchatov Institute in Moscow and at SUNY-Albany, we have begun the testing of this concept with cold neutrons.

We have observed the transmission of cold neutrons through an array of such capillaries bent to radii of curvature as small as 0.4 m. A group of 30 such fibers were cut to a length of 200 mm and laid horizontally, side by side, on a steel ruler. The neutron input end of the fibers was held flat on the ruler and placed in a narrow highly collimated beam, while the other end was moved by a positioning bar at the end of a translational stage. This device enabled us to curve the fibers out of the straight-through beam. Neutron pictures of the beam were taken as the bar was raised successively though small distances. The results demonstrate that the trajectories of neutrons are bent by their passage through the curved capillaries. The non-uniformity of illumination observed demonstrates the need for careful alignment of the capillaries for complete illumination of the entrance to the capillaries to the incoming neutron beam.

A demonstration of neutron focusing has been performed recently by placing nine polycapillary fibers side-by-side on a flat surface. The fibers are spread out onto a cylindrical surface with equally spaced grooves to create a curvature to the fibers, while keeping the entrance of the fibers fixed flat. The bent fibers are then recollected into a conical shape by sliding them through a cadmium ring. The positioning of this aperture determines the location of the focal point. Measurements are taken with the position-sensitive neutron camera at a series of distances from the exit end of the fibers. The results show that the individual outputs come to a small spot at the focus, so that the neutrons are indeed focused! These measurements show clearly the ability to transport cold neutrons through narrow capillaries and to guide their trajectories, and will lead eventually to the focusing of neutron beams using this technique.

9. Instrumental Neutron Activation Analysis of Marine Mammal Tissues from the National Biomonitoring Specimen Bank

R. Demiralp, E.A. Mackey, B.J. Koster, S.A. Wise, P.R. Becker, and T. Lillestolen

The Inorganic Analytical Research Division and the Organic Analytical Research Division continue to support other agencys' projects in specimen banking. There are currently four projects for which samples are being collected, processed and archived in the NBSB. Two of these projects involve marine mammal tissues: 1. the Alaska Marine Mammal Tissue Archival Project (AMMTAP) a project sponsored jointly by National Oceanic and Atmospheric Administration (NOAA) and Minerals Management Service, and 2. the National Marine Mammal Tissue Bank (NMMTB), sponsored jointly by NOAA and National Marine Fisheries Service. For each project, selected subsamples are analyzed shortly after collection for the purpose of real-time monitoring of levels of various organic pollutants and trace elements. The OARD analyzes these tissues for organic constituents such as DDT, DDT metabolites and selected PCB congeners that are indicators of exposure to organic contaminants. The IARD is involved in the characterization of these tissues for trace element composition.

In 1987, the AMMTAP was established and since then tissues from 65 animals have been collected and stored in the bank. Instrumental neutron activation analysis (INAA) has been performed on selected tissues from 12 of these animals, providing concentrations for as many as 36 elements (8 of which were analyzed during this past year). These results were presented at the First International Symposium on Biological and Environmental Specimen Banking and will appear in the document titled "Determination of Inorganic Constituents in Marine Mammal Tissues" in *Science of the Total Environment.* In addition, a five year summary that includes a description of the sample inventory and results of both organic and inorganic analyses is nearing completion. Although relatively few tissues have been analyzed, the INAA data represent one of the most comprehensive data banks for element composition of marine mammal tissues. For several of the elements measured, these are the first results for marine mammal tissue.

In 1990, the demonstration phase of the NMMTB began and by the end of this year liver and blubber tissue from 9 pilot whales and from 10 harbor porpoises had been collected and banked. We are in the process of performing INAA on the liver tissues from these animals. To assist other researchers engaged in marine mammal tissue analysis, NIST has prepared quality assurance (QA) materials from pilot whale liver (for inorganic analyses) and from pilot whale blubber (for organic analyses). INAA was performed on two to six aliquots from each of six different bottles of the this QA liver tissue. Concentrations for 18 elements were determined and results indicated that the material is homogeneous (concentrations were constant within ± 2%) with respect to 13 of these but appears to be inhomogeneous with respect to Al. There are plans to collect more of these materials for the preparation of a fresh frozen NIST SRM for each.

10. Cold Neutron Depth Profiling

G.P. Lamaze, R.G. Downing, J.K. Langland, and S.T. Hwang

The Cold Neutron Depth Profiling (CNDP) facility at Cold Tube West (CTW) became operational on October 31, 1990. The neutron beam is filtered by 13.5 cm of single crystal sapphire, which has the effect of reducing the slow neutron fluence rate by a factor of three, while reducing the fast neutron fluence rate by a factor of about 500. Collimators are located both within the biological shield and in the external-to-the-shield rotating shutter. The shutter is made up of two cylinders whose beam tubes fully align in the beam-open configuration and are non-aligned in the beam-closed configuration to reduce streaming. The collimators in these shutters can be accessed in the beam-closed configuration with the reactor at full power. The diameter and intensity of the neutron beam can then be modified at any time to suit the needs of a particular experiment. The measured neutron fluence rate (capture flux) at the target position, with the 16 mm diameter collimator in place, is 1.2×10^9 $cm^{-2}s^{-1}$. A pancake fission chamber mounted on the entrance port of the NDP chamber provides a run-to-run neutron monitor.

The target chamber was obtained from a commercial vendor using a design developed at NIST. The entire chamber is stainless steel and uses copper gaskets at all but three sealing surfaces, the beam entrance, the exit windows and the opening used for changing samples. This last surface can use either viton o-rings or copper gaskets. In practice, the desire to change samples quickly usually outweighs the need for ultra high vacuum, but the capability to do the latter does exist. The chamber itself is a 61 cm diameter cylinder with access ports in the top and bottom plates as well as through the side walls. The use of standardized flanges allows new features such as in-situ cleaning of samples, time-of-flight measurements, heating and cooling of the sample, and cooling of the surface barrier detectors to be easily added in the future.

The beam enters and exits through 10-cm diameter ports sealed with thin aluminum windows. These can be replaced with sapphire windows if a metal gasket seal is required. The chamber is evacuated with a 180 l/s magnetic bearing turbo molecular pump. This pump was chosen to reduce microphonic effects on the charged particle detectors. The detectors are surface barrier detectors in a ring mount. A rotary base is used to position the charged particle detectors about the axis of the sample. Detectors can be placed at any angle and can be mounted every 10 degrees. Currently, there exists electronics to operate four detectors simultaneously.

Samples (up to 15 cm in diameter) are mounted on a set of motor driven positioners. A rotary base allows the operator to select the angle of the sample with respect to the beam. The ability to rotate the detectors and sample independently allows the detector to be positioned at any angle with respect to the sample without putting the detector in the beam. Mounted on top of the sample rotator are x and y positioners. These have 15 cm of travel each, allowing a full scan of 15 cm diameter samples. All four positioning devices are controlled by a PC compatible microcomputer. A program has been written in BASIC to enable unattended sample scans. The signals from the surface barrier detectors are processed in a standard fashion and the amplified signals are sent to Analog-to-Digital converters interfaced with a multiuser minicomputer. This computer can simultaneously process data from both the thermal and cold NDP facilities. Spectra from these computers can then be transferred to a variety of other computers for data reduction, plotting, etc.

A recent spectrum of a sample of Cobalt-Nickel Oxide (^{17}O enriched) taken at the CNDP facility is, to our knowledge, the first nondestructive determination of near-surface oxygen made by NDP anywhere in the world. The ability to obtain oxygen profiles is a significant addition to the elements that are now analyzed routinely at NIST: boron, lithium, nitrogen, and helium.

11. Prompt-Gamma Activation Analysis With Cold Neutrons

R.M. Lindstrom

A permanent, full-time instrument for prompt-gamma activation analysis (PGAA) is being constructed as part of the Cold Neutron Research Facility (CNRF). As a result of a compact sample-detector geometry, the sensitivity (counting rate per gram of analyte) is a factor of four better than the existing Maryland-NIST instrument. Hydrogen backgrounds of a few tens of micrograms have already been achieved, which promises to be of value in numerous applications where quantitative nondestructive analysis of small quantities of hydrogen in materials is necessary. Further reduction by one to two orders of magnitude is probable in the near future.

Experience gained from more than a decade's operation of the Maryland-NIST thermal instrument, and with a system at the German research center in Jülich, has been incorporated in the design of the instrument at the CNRF, to give high gamma detection efficiency, low background (particularly for hydrogen), and facile operation. The instrument is installed on neutron guide NG-7 in the CNRF hall. A filter of 152 mm of single-crystal Bi and 127 mm of Be, both at liquid nitrogen temperature, is installed in the guide 3.1 m upstream from the PGAA sample position.

Several measurements have been made in the short time that this cold-neutron instrument has been in operation. The first measurement with cold neutron PGAA in the CNRF was the determination of hydrogen in a sample of C_{60} fullerene, "buckyballs", intended for neutron scattering studies. Cold-neutron PGAA found a hydrogen concentration of 0.92 ± 0.09 wt %, which was too high for satisfactory scattering measurements. After repurification of the material, hydrogen was measured again. A 600-mg sample, contained in the aluminum sample holder intended for the scattering measurements, was irradiated in the PGAA beam for 100 minutes live time. The sample was surrounded with a flowing atmosphere of He contained in a Teflon tent. A clear H peak was visible at more than ten times the intensity of a blank sample of spectroscopic grade graphite. The sample contained 0.077 ± 0.014 wt % H, which was adequately low for the neutron scattering measurements. In other work, hydrogen was measured in a Pr_2CuO_4, a superconductor analog; a 1-h irradiation gave a concentration of 0.017 ± 0.010

wt % H. Hydrogen was determined in a 50-nm borophosphosilicate glass film on a quarter of a 10-cm silicon wafer; an upper limit of 2 μg/cm^2 was found.

Future enhancements to the counting system will include a Compton suppressor, an automatic sample changer, and a second detector system, which will permit gamma cascade coincidence measurements. The difficulties associated with working adjacent to the upper guide -- restricted space and Si capture background--may be ameliorated in the future by deflecting the PGAA beam away from the guide. Additional improvement in sensitivity is possible since neutron optics can be used to focus cold neutrons onto a small area. Gains of an order of magnitude in fluence rate may be obtainable.

12. Automated High-Precision Coulometry

K.W. Pratt and W.F. Koch

Constant-current coulometry is the method of choice for assays of high-purity reagents where maximum precision and accuracy (10-100 ppm relative) are required. The manual technique, developed and refined at NIST over a 30-year period, demands a high degree of skill and close attention to minute detail. Additionally, manual procedures are subject to variations in technique that can result in significant systematic errors which are difficult to quantitate. Automation of the technique will reduce these systematic errors, accelerate the learning curve for new personnel, and reduce the tedium of the procedure.

Research to automate these procedures was initiated in FY91. During this period, feasibility was demonstrated for each fundamental automated operation: weighing, dissolution, solution handling, current control, endpoint determination, and statistical evaluation of the experimental results. Linking of these individual operations to produce the entire analytical procedure was also achieved. Initial tests with actual analyses are in progress.

The control program structure for high precision coulometry is based on operational modules (subprograms), each of which directs a specific operation required for the analysis. Individual modules belong to one of two levels. High-level modules, e.g., "rinse the cell" or "determine the amperometric endpoint," relate directly to steps in the chemical analysis. Instrumental modules, e.g., "open valve 21 for 0.47 minutes" or "turn off the stirrer," effect specific hardware or I/O device operations. As a result of this program organization, newly-developed assay procedures or refinements to existing procedures can be readily implemented. For example, if a refined endpoint determination is developed, only the endpoint module needs to be altered.

The endpoint determination and sample introduction are the heart of the program. The endpoint determination detects a preliminary endpoint, then rinses the cell and rechecks the endpoint for any systematic error. The final value for the endpoint is determined only after no change is noted on rinsing. In addition, any undetected systematic errors present in the endpoint determination are eliminated by using the identical procedure for endpoint detection before and after the main sample titration.

The sample introduction step calculates a preliminary titration time based on the approximate sample weight that is used for timing the main, high current titration. This time is based on the weight difference between the empty weighing vessel and the vessel plus sample weight. The main titration is initiated after the sample is introduced into the cell and proceeds while the final vessel weight is obtained. When the final weight is entered, the main titration time is recalculated, based on the actual difference. This procedure corrects for any sample remaining in the weighing vessel after sample introduction.

The present program has been designed for the constant-current coulometric titration of $K_2Cr_2O_7$, KCl, NaCl, As_2O_3, and strong acid solutions. Feasibility will be demonstrated for these compounds during FY92. It is anticipated that the automated system will be used in the near future to assay these compounds for certification of renewal SRMs.

13. A New pH Buffer for Clinical Measurements

Y.C. Wu, D. Feng, W.F. Koch, and L.A. Holland

The measurement of pH in the clinical setting is of major importance to the proper diagnosis and treatment of life-threatening physiological conditions. For the last several decades the clinical community has relied on two NIST buffers to calibrate pH measurement systems. These buffers are based on admixtures of disodium hydrogen phosphate and potassium dihydrogen phosphate. It has long being recognized that calibration with these phosphate buffers for clinical applications (i.e., measurement of pH in blood) results in a constant and reproducible bias of about 0.02 pH units. This bias is due to residual liquid junction potential resulting from the large differences in ionic strength between the phosphate buffer solutions and blood. In addition, new clinical instrumentation that incorporates multi-sensor technology capable of simultaneously quantitating several blood electrolytes, blood gases and pH, is often incompatible with phosphate solutions due to interferences, especially for calcium. Based on these demonstrated needs, we have undertaken a program to develop and certify new buffers that minimize or eliminate the shortcomings of the phosphate buffers.

This year we have completed the research leading to the certification of a second zwitterionic buffer system to complement the zwitterionic buffer (HEPES/HEPESate, pH ≈7.5) issued as an SRM two years ago. The new system is based on the amino acid, 3-(N-morpholino)-2-hydroxypropane sulfonic acid, (MOPSO) and its sodium salt, MOPSOate; the nominal pH of this buffer system is 6.8. In addition to certifying the pH of admixtures of MOPSO/MOPSOate/NaCl at varying concentrations, using the emf method in a Harned-type cell without liquid junction, we have investigated the interactions of the zwitterionic buffer with NaCl and HCl, and we have redetermined the first and second dissociation constants (pK_1 and pK_2) of MOPSO.

The pK_1 was determined by the conductimetric method, which is the first time this method has been used for amino acids. The conductimetric method affords higher accuracy and precision than the emf method in the determination of the dissociation constants in moderately strong acids. MOPSO is an unusual amino acid in that it falls in this class. The investigation into the interactions between MOPSO and HCl has clearly demonstrated that MOPSO in HCl solutions is not a dipole molecule, as are most zwitterionic molecules (including HEPES), but is an ionic entity. We have determined the pK_1 to be 0.061 ± 0.005. The details of these investigations have been reported in three publications.

It should be noted that the HEPES and MOPSO buffer standards are not limited to clinical applications, but are useful as calibrants in moderately high ionic strength situations (such as seawater), and as alternatives for the phosphate solutions in other applications. Our research on the development of new pH buffer standards will continue in an effort to provide more accurate measurements in complex matrices. At present, this effort is focussing on a third zwitterionic buffer with a nominal pH of 7.8, to bracket the normal physiological range.

14. Comparison of X-Ray Fluorescence and Spark Optical Emission for Metal SRM Concentration Profiling

P.A. Pella and M.L. Salit

Historically, metal SRM candidate materials have been assessed for their elemental concentration homogeneity with Spark Optical Emission Spectrometry (OES), with final "piece-to-piece" homogeneity being confirmed with X-Ray Fluorescence (XRF). Relative to Spark OES, XRF offers significant advantages of unattended automated sample handling and the potential for more precise measurement. These factors are driving the industrial shift towards XRF, as well as our emphasis on the use of XRF in the SRM characterization program.

The integration of the two techniques for homogeneity testing of candidate SRM materials into a cohesive program required work in two areas: (1) development of a single report format for the homogeneity testing results from both techniques, and (2) evaluation of differences between the XRF and OES techniques for this application. The first of these developments has been achieved, and the second is ongoing.

The evaluation of homogeneity is now performed with an *Analysis of Variance* test, or ANOVA. Prior to the development of the new evaluation scheme, the homogeneity testing was accomplished using different (NIST written) software programs. The new approach uses a commercially available software package that employs significantly more graphical data analysis more flexible in the forge of statistical models allowed, and is better suited to automatic report generation. The new report has three areas: a run sequence plot, a homogeneity control chart, and tabular statistical results. The run sequence plot is used to assess measurement 'drift' in the experiment. The homogeneity control chart includes the mean, measured data markers encoded to indicate sample identification and the 95% Confidence Interval as a shaded area. These plots are both applicable to the several different but similar types of homogeneity experiments required for support of the metals SRM program. The tabular statistical report includes a table of summary statistics (mean, standard deviation, RSD, minimum and maximum), an *ANOVA* table, and a *Multiple Comparison of Means* tests, which is a tabular-graphical statistical test that shows data groupings. Condensation of the data analysis to a single page per element is intended to make interpretation of the results straightforward, with the graphical section designed to allow meaningful chemical observations to be made in a straightforward manner.

The initial examination of results comparability was made with historic data. The significant observation is that the results are biased differently, but that positional trends in heterogeneity correlate well between results of the two techniques. In this examination, XRF and OES results from the analysis of the final pieces of SRM 1763, a low alloy steel, were overlaid for 2 elements, Mn and Zr. The Mn results indicated *no bias* between the techniques, with strong correlation of the concentration variation trend. The Zr results demonstrate *different bias* between the techniques with OES biased low relative to XRF. Again, strong correlation of the concentration variation trend is observed.

Comparison of the two techniques is ongoing with materials currently under study as candidate SRMs. These will include high temperature alloys, brasses and bronzes. The preliminary results indicate that a combination of XRF and OES, selected for the different materials, elements of interest, and programmatic opportunities will enhance the ability to provide appropriate technical support for the metals SRM program.

15. Slurry Sample Introduction in Graphite Furnace Atomic Absorption for Ultra-Trace Analysis

M.S. Epstein

The determination of ultra-trace transition metal concentrations in high-purity chemicals is perhaps the most challenging problem that can be encountered by an analytical chemist. The combination of low analyte concentration, high matrix concentration, and the ubiquitous nature of transition metals leads to problems with detection, interferences and contamination for most instrumental methods. Graphite furnace atomic absorption spectrometry (GFAAS) is certainly no exception to this rule when applied in the normal configuration of liquid sample introduction after external sample preparation. However, the use of the slurry sample introduction method, in which a suspension of the chemically-untreated sample is introduced directly into the furnace, can overcome many of the problems encountered in the conventional use of GFAAS for difficult analyses.

The specific analytical problem was the determination of iron, nickel, copper and cobalt at the ng/g level in high-purity aluminum fluoride, a precursor in the manufacture of glass for fiber optic use. Aluminum fluoride is difficult to dissolve and iron contamination is impossible to avoid when any chemical sample preparation is involved. Our approach to this problem was to investigate the conditions under which the sampling system used for slurries of less than 1% solids content could quantitatively transport very high percent (i.e., 50%) suspended solids. Parameters of importance were the inner diameter and immersion depth of the sampling tube, the duration and application rate of the furnace drying and charring temperatures, the flow rate of the argon purge gas, the use of a highly-accurate background correction system, and the use of the method of standard addition for quantitation. Optimization of these parameters provided quantitative transfer of suspended sample from the autosampler cup to the furnace and satisfactory signal reproducibility. The procedure gave an effective dilution factor of 2x, rather than the typical 20x to 100x dilution used for conventional sample preparation or slurry analysis. Detection limits were less than 10 ng/g for all four elements, and nickel, iron and copper were quantitatively determined in several different samples of aluminum fluoride. Although no comparative results from other analytical methods were available for these samples, the contaminants were in the expected concentration range. This simple slurry-sampling method should be readily applicable to the rapid determination of ultra-trace metals in a variety of solid materials.

16. Use of UV-VIS Fourier Transform Spectroscopy as a Diagnostic Tool for Optical Emission Sources

J.C. Travis and M.C. Salit

After a year of debugging, the NIST UV-visible Fourier transform spectroscopy (FTS) system is demonstrating utility in its second year of operation. The commercial Chelsea Instruments FT-500 was purchased to support the group research effort in emission spectroscopy because of its very high resolving power (10^6), wavelength accuracy (better than 1 part in 10^6), and broad spectral bandwidth. This year the instrument was optically coupled to a dedicated Inductively Coupled Plasma (ICP) source and a large volume of data was acquired. Preliminary studies were also performed with a demountable glow discharge lamp, and a new lamp has been designed for construction this year.

Initial studies with the ICP were directed toward the optimization of instrumental operating parameters for acquiring a spectral library representative of at least 40 important elements and covering a broad spectral range. The spectra are an integral part of a postdoctoral research program to explore the application of artificial neural networks to the interpretation of complex atomic spectra of mixtures of elements. Spectra acquisition was begun late in the fiscal year, and some 30 spectra were acquired by year's end. The results of the neural net study will be reported next year, but the spectral library has already provided impressive evidence of the diagnostic power of the instrument to provide research support for ICP emission spectroscopy.

One of the goals of the FTS/ICP program is to support the call of prominent spectroanalytical chemists for an electronically accessible data base specifically constructed for the atmospheric argon ICP. The FTS is ideally suited to provide superior absolute wavelength accuracy and fully resolved spectral profiles for major spectral lines, but is not capable of providing the dynamic range (10^5 - 10^6) needed to fully characterize potential spectral matrix interference lines as well as lines used for quantitation. A major question answered by the spectral library is whether the dynamic range of 10^3 specified for the FTS with an ideal (stable) source would be severely degraded by the well-known multiplicative (flicker) noise of a conventional ICP with liquid aerosol sample introduction. The gratifying answer provided by the data is that a dual-channel noise cancellation feature of the instrument design is capable of providing a linear dynamic range (LDR) of ~500 under adverse circumstances. Therefore, it will be possible to engage in a proposed collaboration with Iowa State University, in which the NIST FTS would provide enough spectral data to be able to calibrate the Ames high resolution diode array spectrometer at 6-angstrom intervals.

A second important spectral diagnostic in support of conventional ICP/OES is the complete resolution (limited solely by Doppler and pressure broadening) of complex spectral profiles resulting from hyperfine structure and/or isotopic effects. A number of important spectral lines, as seen from the library, have significant spectral structure in comparison to the environmental broadening. Theoretically-based hyperfine/isotopic multiple-line patterns can be curve-fitted to these profiles, and the resulting profiles can be convolved with instrument functions for lower resolution grating instruments. Such detailed profile data in modern, computerized, scanning instruments, could provide recognition of spectral interference in the presence of complex line profile.

Other diagnostic functions of the instrument for the ICP include Boltzman measurements of effective electronic temperature, Doppler width measurements of kinetic temperature, line splittings due to electric and magnetic fields, line shifts due to electric fields and/or pressure effects. Tentative Boltzman measurements were made by a totally computerized comparison of Fe data with electronic NIST tables of transition probabilities, and further studies of all of these functions will be pursued in the coming year. Similar diagnostic functions will also be investigated in the glow discharge.

17. Verification of Stoichiometry of Primary Materials Used in the Preparation of Spectrometric Solution SRMs

C.M. Beck II and T.A. Butler

NIST currently offers for sale, through the Standard Reference Materials Program, a suite of about 70 single-element Spectrometric Standard solutions with a concentration of 10,000 µg/mL ±0.4% relative. For rare-earth elements, the cost of using the high-purity metal in preparing the SRM is prohibitive, and a less-expensive compound (usually an oxide) of the appropriate element is used. The stoichiometry of each of these compounds must be verified at the time the spectrometric solution is prepared. The SRM solution is prepared from the compound in a 4-liter batch, and before bottling, an aliquot of the batch is compared with a pure-metal primary standard using classical analysis. In this way the stoichiometry of the compound used in preparing the SRM can be established to an accuracy of 0.1%-0.2% relative. Using titrimetry, we have compared SRM solutions made from high-purity oxides with their pure-metal counterparts for the following elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy.

Since the primary metal standards used have been analyzed for *most* elements and contain <100 ppm impurities, a high-precision gravimetric or titrimetric comparison is sufficient to establish the stoichiometry. For example, the following general procedure is used for the rare earths (except Ce). Three 10.00-mL aliquots of a 10,000-µg/mL Spectrometric Standard SRM are titrated with EDTA in a solution appropriately buffered to ±0.01 pH units (usually optimized between pH=5 and pH=6 in order to obtain the sharpest endpoint). Typically, the three titrations will agree to within 0.02% - 0.04% relative. Then, using the same 10.00-mL transfer pipet, three 10.00-mL aliquots of a 10,000-µg/mL, pure-metal standard are titrated with the same EDTA solution under identical conditions. These three titrations will also usually agree to within 0.02% - 0.04%. The averages of the triplicate runs on each solution are used as a comparison of the concentrations of the metal in each of the two solutions, provided that previous instrumental analysis has ruled out the presence of gross amounts of interfering elements in the solution prepared from the compound. Since each average has an uncertainty of only a few parts in ten thousand, a relative difference *between* the two solutions of 0.1% - 0.2% is easily seen. In the case of Ce, a redox titration was used instead. Using this principle, other spectrometric solution SRMs made from compounds can be compared with pure-element primary standards to verify stoichiometry.

18. Stoichiometry of Superconductor Materials by ICP-OES

R.L. Watters, Jr. and L.J. Wood

Compositional analysis provides essential information for understanding the physics of high-temperature superconductors, and for developing the production processes that will be required for their industrial application. In addition to microstructural information, two kinds of bulk chemical analyses are required: accurate determination of the stoichiometry, and sensitive determination of the impurities in the superconductor test specimens and in the precursor materials from which superconductors are synthesized. For the chemical determination of stoichiometry, it would be highly desirable to be able to measure oxygen accurately so that the crucial oxidation number can be known directly. No direct analytical methods are available which offer sufficient precision and accuracy to distinguish between 6.9 and 7.0 oxygen atoms per yttrium atom. In this work, the main constituents in $YBa_2Cu_3O_7$ were determined by inductively coupled plasma emission spectrometry (ICP-OES).

Samples of the superconductor precursor material (coprecipitated yttrium, barium, and copper hydroxycarbonates) were analyzed by ICP-OES to determine the three major elements and to estimate sources of variability in the measurement process. Since the overall relative uncertainty of the determinations of Y, Ba, and Cu were expected to be less than 1%, the analysis was designed to evaluate sources of error which are usually too low to be important in a trace analysis application. These sources of error include dilution, calibration, spectrometer resolution, and wavelength scanning accuracy. The latter two effects are convolved into a generalized monochromator effect, which probably has more to do with scanning accuracy than spectral resolution since the spectral lines are free of interferences. In addition, sample homogeneity was evaluated. These sources of variance were compared to the instrumental replication error to determine their significance. Calibration effects, sample homogeneity, and dilution effects were treated as random components of variance to be evaluated by classical ANOVA methods.

Duplicate observations for Y in each of five samples and two calibrations for each yielded twenty results for the ANOVA. Calibration effects and sample–to–sample variance were estimated by the ANOVA, and the number of effective degrees of freedom (r) for the estimate of the overall standard error was calculated. A small sample effect was detected, which suggests sample inhomogeneity at the 100–mg sample size. The relative standard error of the mean for Y is less than 1%, and the difference between the means for the two monochromators is not significant.

In the case of Cu, the components of variance included in the standard error of the mean were replication error and sample–to–sample variance. The effects of sample inhomogeneity were less pronounced for copper than for barium, and the results from each monochromator were nearly identical. The relative standard error was less than 0.5%.

For the Ba determination, each sample solution was diluted by a factor of ten and included in the analysis to evaluate the variance due to volumetric dilution. The ANOVA revealed neither dilution nor calibration effects, leaving only the sample and instrument replication effects to be included in the estimate of the standard error of the mean. The relative standard error of the mean was also less than 0.5%.

The actual oxygen content of these precursor materials is not stoichiometric. If similar analyses were performed on calcined material, the resulting estimate of oxygen obtained by subtraction from 100% will have a relative error of about 1%. In a superconductor compound with a nominal 7 moles of oxygen, the uncertainty would be 0.07 moles.

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Downing, R.G., "Analytical Measurements Using Neutron Beam Techniques," International Atomic Energy Agency, Korea Standards Research Institute, Taejon, Republic of Korea, September 30, 1991.

Feng, Daming, "Investigation of the Interaction of Sodium Chloride and Two Amino Sulfonic Acids; HEPES and MOPSO by EMF Measurements," American Chemical Society Meeting, New York, NY, August 27, 1991.

Greenberg, R.R., "Prompt Gamma Activation Analysis," Workshop on Applications of Cold Neutron Spectroscopy in Chemistry, Bldg. 235, B108, Gaithersburg, MD, June 6, 1991.

Greenberg, R.R., "The Role of Nuclear Methods in the Certification of Elemental Concentrations in NIST Standard Reference Materials," 27th Colloquium Spectroscopicum Internationale, Bergen, Norway, June 14, 1991.

Greenberg, R.R., "Neutron Activation Analysis With Chemical Separations," International Congress on Analytical Sciences, Chiba, Japan, August 31, 1991.

Greenberg, R.R., Becker, D.A., Lindstrom, R.M., and Blackman, M.J., "A Retrospective Look at Interferences in Neutron Activation Analysis," Modern Trends in Activation Analysis, Vienna, Austria, September 20, 1991.

Greenberg, R.R., "High Accuracy Analysis of NIST Standard Reference Materials Using Neutron Activation Analysis," Joint Research Center, ISPRA, Italy, September 27, 1991.

Iyengar, V.C., Clarke, W.B., and Downing, R.G., "Boron and Lithium in Total Mixed Diets of Countries Participating in the IAEA Project on Dietary Intake of Minor and Trace Elements," Modern Trends in Activation Analysis, Vienna, Austria, September 16, 1991.

Kelly, W.R., "Multi-Variable Experiments and Applications to Radioanalysis," 36th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, Oak Ridge, TN, October 22, 1990.

Kelly, W.R., "Improved Measurement of Particulate Dry Deposition With Enriched Rare-Earth Isotopes," December 1, 1990.

Kelly, W.R., "Determination of Sulfur in Coals by Isotope Dilution Thermal Ionization Mass Spectrometry," ASTM Meeting of D-5, Charlotte, NC, May 22, 1991.

Kelly, W.R., "Tagging Diesel and Residential Oil Furnace in Roanoke, Virginia With Enriched Isotopes of Samarium," Vancouver, Canada, June 23, 1991.

Kelly, W.R., "Determination of Sulfur in SRM Oils by Isotope Dilution Thermal Ionization Mass Spectrometry," ASTM Meeting of D-2, Toronto, Canada, June 26, 1991.

Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems," Dow Analytical Science Discussion Group, Midland, MI, November 14, 1990.

Kramer, G.W., "A Critical Look at Robots in the Laboratory," NRC Ocean Studies Board Meeting, Irvine, CA, January 7, 1991.

Kramer, G.W., "A Common Data and Control Interface for Analytical Chemistry Instrumentation," 42nd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, March 8, 1991.

Kramer, G.W., "What Do We Really Want in a Standard Interface for Laboratory Equipment?," Spectroscopy Society of Canada Symposium on Sample Preparation for Inorganic and Organic Analysis, Toronto, Canada, May 16, 1991.

Kramer, G.W., "Standardization in Laboratory Automation: A Technological Necessity," First International Conference on Robotics in Laboratory Medicine, Charlottesville, VA, July 27, 1991.

Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems," Scientific Computing and Automation Conference, Philadelphia Convention Center, Philadelphia, PA, September 24, 1991.

Lamaze, G.P., "The New Cold Neutron Depth Profiling Instrument at NIST," Methods and Applications of Radioanalytical Chemistry II, Kona, HI, April 23, 1991.

Lindstrom, R.M., "A Low-Background Gamma-Ray Assay Laboratory for Activation Analysis," Canberra-Nuclear Data Users' Meeting, Washington, DC, October 24, 1990.

Lindstrom, R.M., "High-Sensitivity Gamma Counting in Activation Analysis," International Committee for Radiation Metrology Symposium on Low-Level Measuring Techniques and Alpha Particle Spectrometry, Monaco, Monaco, June 6, 1991.

Lindstrom, R.M., "Neutron Capture Prompt Gamma-Ray Activation Analysis at the NIST Cold Neutron Research Facility," 8th International Conference on Modern Trends in Activation Analysis, Technical University of Vienna, Atominstitute of the Austrian Universities, Vienna, Austria, September 16, 1991.

Lindstrom, R.M., "The NIST Cold Neutron Research Facility and Prompt-Gamma Activation Analysis," Central Research Institute for Physics, Budapest, Hungary, September 23, 1991.

Mackey, E.A., "Use of Spherical Targets to Insure Accuracy in Neutron Capture Prompt X-Ray Activation Analysis of Hydrogenous Materials," 8th International Conference on Modern Trends in Activation Analysis, Technical University of Vienna, Atominstitute of the Austrian Universities, Vienna, Austria, September 16, 1991.

Mackey, E.A., "Scattering and Absorption Effects in Neutron Beam Activation Analysis Experiments," 8th International Conference on Modern Trends in Activation Analysis, Technical University of Vienna, Atominstitute of the Austrian Universities, Vienna, Austria, September 16, 1991.

Messman, J.D., "Inexpensive PC-Based Data Acquisition Interface for Determining Carbon and Sulfur in Steel Samples by Combustion-Evolved Gas Analysis," 17th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Cleveland, OH, October 9, 1990.

Messman, J.D., "Use of Optical Filter Standard Reference Materials for Ultraviolet and Visible Spectrophotometry," invited tutorial workshop, The Upjohn Company, Kalamazoo, MI, November 8-9, 1990.

Messman, J.D., Technical Status of Optical Filter Standard Reference Materials for UV/VIS Absorption Spectrophotometers," National Conference of Standards Laboratories Workshop and Symposium, Albuquerque, NM, August 21, 1991.

Messman, J.D., "Use of Optical Filter Standard Reference Materials for Ultraviolet and Visible Spectrophotometry," invited tutorial workshop, Ethicon, Inc., Chicago, IL, September 24, 1991.

Mildner, D.F.R., "Focusing of Neutrons," Department of Physics, San Jose State University, San Jose, CA, October 18, 1990.

Mildner, D.F.R., "Focusing of Neutrons," Reactor Radiation Division, NIST, Gaithersburg, MD, May 21, 1991.

Mildner, D.F.R., "Focusing of Neutrons," Cold Neutron Facility, NIST, Gaithersburg, MD, July 17, 1991.

Mildner, D.F.R., "Neutron Focusing Using Converging Guides," 7th International Symposium on Capture Gamma-ray Spectroscopy and Related Topics, Pacific Grove, CA, October 15, 1990.

Pella, P.A., "Fabrication and Selected Applications of a NIST X-Ray Microfluorescence Spectrometer," Pacific-International Congress on X-Ray Analytical Methods, Hilton Hawaiian Village Hotel, Honolulu, HI, August 15, 1991.

Petersen, J.V., "The Consortium on Automated Analytical Laboratory Systems--An Update on Progress Made," Scientific Computing and Automation Conference, Philadelphia, PA, September 24, 1991.

Salit, M.L., "Strategies for Extracting Chemical Information from an ICP-FTS System," The Pittsburgh Conference, Chicago, IL, March 5, 1991.

Smith, M.V., "Certification of Optical Transmittance SRMs for Spectrophotometry," 33rd Rocky Mountain Conference on Applied Spectroscopy, Radisson Hotel, Denver, CO, July 30, 1991.

Smith, M.V., "Time Stability of Optical Transmittance Filters," Poster Paper 262P, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, March 4, 1991.

Travis, J.C., "Preliminary Studies in UV/Visible Fourier Transform Spectrometry at the National Institute of Standards," Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XVII), Cleveland, OH, October 11, 1990.

Travis, J.C., "Ionization Techniques for Ultrasensitive and Selective Chemical Analysis," Alkemade Memorial Symposium, Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XVII), Cleveland, OH, October 11, 1990.

Travis, J.C., "Selective Laser Ionization for Atomic Spectrochemical Analysis," Departmental Seminar, Department of Chemistry, Clemson University, Clemson, SC, November 27, 1990.

Travis, J.C., "Characterization of Fourier Transform Spectroscopy of Analytical Emission Sources," 37th Canadian Spectroscopy Society Conference, Ottawa, Canada, August 12, 1991.

Turk, G.C., "Imaging of the Active Flame Volume for Laser-Enhanced Ionization," FACSS, Cleveland, OH, October 10, 1990.

Turk, G.C., "Laser-Enhanced Ionization of Flames and Plasmas," Department of Chemistry Indiana University of Pennsylvania, Indiana, PA, December 7, 1990.

Vetter, T.W., "Use of Instrumental Techniques to Improve Gravimetric Analysis of Aluminum," 17th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Chicago, IL, October 10, 1990.

Vocke, R.D., Boron Isotopic Studies of Geothermal Fluids," American Geophysical Union 1990 Fall Meeting, San Francisco, CA, December 5, 1990.

Vocke, R.D., "Proposal to Develop An Internal Standard Method for Rapid and Accurate Pb in Whole Blood," California Public Health Meeting, Emoryville, CA, January 25, 1991.

Vocke, R.D., "High Precision Li and B Isotopic Analyses in a Variety of Natural Matrices," ESS Department, University of New York, Stony Brook, NY, April 5, 1991.

Vocke, R.D., "Boron Isotopic Studies of Hydrothermal Fluids," GAC-MAC-SEG, Toronto, Canada, May 27, 1991.

Vocke, R.D., "Lead Isotopic Variations in Archaeometry: A Geochemistry Perspective," Smithsonian Institution, Washington, DC, June 3, 1991.

Watters, R.L., Jr., "The Use of Standard Reference Materials in Spectrometric Analysis Quality Assurance Programs," Fifth Italo-Hungarian Symposium on Spectrochemistry-Quality Control and Assurance in Life Sciences, Pisa, Italy, September 10, 1991.

Wythoff, B.J., "Spectral Peak Detection With a Multi-Layered Neural Network," Eastern Analytical Symposium, Garden State Convention and Exhibit Center, Somerset, NJ, November 13, 1990.

3. Committee Assignments

C.M. Beck II

ASTM, E01, Chemical Analysis of Metals, Ores, and Related Materials
ASTM, E01.02, Ores, Concentrates, Slags, and Refractories

D.A. Becker

ANS, SC.01, Trace Element Analysis Committee
ANS, SC.16, Isotopes and Radiation
ANS, SC.16, WG.01, Activation Analysis
ANS, C004, Biology and Medicine
ANS, C006, Standards Steering Committee
ASTM, E-10, Nuclear Technology and Applications
ASTM, 10.05, WG.08, Nuclear Environmental Metrology
ASTM, D-19, Water
ASTM, 19.01, Statistical Methods
ASTM, 19.02, General Specification and Technical Resources
ASTM, 19.03, Sampling of Water and Water-Formed Deposits and Surveillance of Water
ASTM, 19.04, Methods of Radiochemical Analysis
ASTM, 19.05, Inorganic Constituents in Water
ASTM, 19.07, Sediments Chairman
ASTM, E10.05, Nuclear Radiation Metrology
ASTM, E10.05, WG.10, Neutron Metrology
ASTM, E10.05, WG.12, Nuclear Methods of Chemical Analysis

D.S. Braverman
Society of Applied Spectroscopy, Baltimore/Washington Section (Treasurer)

J.R. DeVoe
EPA Special Interagency Task Subgroup on Method Development and Standards for Lead Analysis (Chairman)
Work Group C, 1st National Conference: Laboratory Issues in Childhood Lead Poisoning Prevention sponsored by the Association of State and Territorial Public Health Laboratory Directors (ASTPHLD) (Chairman)

R.G. Downing
ASTM, FOO1, Electronics
ASTM, F001, WG.11, Alpha Particle Induced Soft Errors
ASTM, E10.05, WG.12, Nuclear Methods of Chemical Analysis
CSTL Seminar Committee

M.S. Epstein
ASTM, D-19, Water
Project Study and Advisory Committee, Society for Applied Spectroscopy (Chairman)
Professional Development Program, Baltimore-Washington Section of Society for Applied Spectroscopy (Chairman)
Tollers Committee, Society for Applied Spectroscopy
Board of Directors, National Capital Area Skoptics

R.F. Fleming
ASTM, 10.05, Nuclear Radiation Metrology
ASTM, 10.07, Radiation Effects on Materials
ASTM, WG.04, Radiation Metrology for Food Processing

R.R. Greenberg
ASTM, E10, Nuclear Technology and Applications
ASTM, E10.05, Nuclear Radiation Metrology
ANS, Trace Analysis Committee, Division of Biology and Medicine
ANS, Executive Board, Division of Biology and Medicine
NIST Radiation Safety Committee

W.R. Kelly
NIST Colloquium Committee (Chairman)

H.M. Kingston
ASTM, E49, Computerization of Material Property Data
ASTM, E49.52, Experimental Data Interchange
ASTM, E31 Computerized Systems
ASTM, E31.40, Laboratory Information Management Systems

IUPAC, 005, Analytical Chemistry
IUPAC, C.05.3, Analytical Nomenclature

W.F. Koch
NCCLS, C004, Board of Directors
NCCLS, CO16, National Committee for Clinical Laboratory Standards
ASTM, D-19, Water
ASTM, D-22, Sampling and Analysis of Atmospheres
ASTM, 22.06, Ph in Atmospheric Deposition
ASTM, SC.02, General Specifications and Technical Resources
ASTM, SC.02, Clinical Standards
AWWA, C002, Standards Methods
AWWA, SC.05, Inorganic Constituents in Water
IUPAC Chem, V.5, Commission on Electroanalytical Chemistry

G.W. Kramer
ASTM, E31, Computerized Systems
ASTM, E31.40, Laboratory Information Management Systems
ASTM, E49, Computerization of Material Property Data
ASTM, E49.52, Experimental Data Interchange

G.P. Lamaze
ASTM, EO10, Nuclear Technology and Applications
ASTM, E10, SC.05, Nuclear Radiation Metrology
ASTM, E10, SC.94, Membership Subcommittee, Nuclear Technology and Applications

J.K. Langland
NIST Electronics Storeroom Committee (Chairman)

R.M. Lindstrom
NIST Radiation Safety Committee
NIST Reactor Safety Evaluation Committee

J.D. Messman
SAS Audit Committee (Chair-elect)
ASTM, E13.01 Subcommittee on UV/Vis Spectrophotometry

J.R. Moody
ASTM, D-19, Water
ASTM, 19.05, Inorganic Constituents in Water
ACS, C002, American Chemical Society Committee on Analytical Reagents
IUPAC Sub-commission on Isotopic Abundance Measurements (Chairman)
Society for Applied Spectroscopy, Baltimore/Baltimore Section (Chairman)
CSTL Quality Assurance Committee

P.A. Pella

ASTM, E.01 Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, E01.22 Statistics and Quality Control

K.W. Pratt

NIST Research Information Center, Division 834 Subject Specialist
Inorganic Analytical Research Division Seminar Committee
Inorganic Analytical Research Division High Purity Reagents Committee

M.V. Smith

ASTM, E13.01, Ultraviolet and Visible Spectroscopy

G.C. Turk

IUPAC, V.4 Commission on Spectrochemistry
Inorganic Analytical Research Division Seminar Committee

T.W. Vetter

ASTM, E01 Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, E01.01 Irons, Steels, and Ferroalloys
ASTM, E01.02 Ores, Concentrates, and Related Metallurgical Materials
ASTM, E01.23 Terminology
ASTM, E01.24 Editorial and Publications
ASTM, E02.01 ISO TAG on Concentrates

R.D. Vocke

Panel Member, Work Group C, 1st National Conference: Laboratory Issues in Childhood Lead Poisoning Prevention sponsored by the Association of State and Territorial Public Health Laboratory Directors (ASTPHLD)

R.L. Watters, Jr.

Society for Applied Spectroscopy National Nominating Committee
Federation of Analytical Chemistry & Spectrometry Society Governing Board
ASTM, E01, Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, E01.01, Iron, Steel, and Ferroalloys
ASTM, E01.22, Statistics and Quality Control, Vice Chairman

Y.C. Wu

ASTM, D19, Water
ASTM, D19.05, Inorganic Constituents in Water
ASTM, SC.09, Saline and Brackish Waters

4. Other

a. Editorships

M.S. Epstein

Editorial Advisory Board, Journal of Analytical Atomic Spectroscopy

Guest Editor, Special Issue of Spectrochimica Acta B on Reference Materials and Reference Methods

H.M. Kingston

Laboratory Robotics and Automation

G.W. Kramer

Laboratory Robotics and Automation
Intelligent Instruments and Computers
Journal of Chemical Information and Computer Science
American Chemical Society, Computer Buyer's Guide

P.A. Pella

Member of Advisory Board, "X-Ray Spectrometry," An International Journal Published by John Wiley and Sons, Limited, West Sussex, England

J.C. Travis

Editorial Advisory Board, Spectrochemica Acta B

G.C. Turk

Editorial Board, Atomic Spectrometry Updates

b. Seminars

October 3, 1990

Jerry Liesegang, PE Nelson, Norwalk, CN, "Laboratory Information Management Systems and Instrument Interfacing at PE Nelson." (Division Sponsor: G.W. Kramer)

October 5, 1990

James S. Langer, Institute of Theoretical Physics, University of California, Santa Barbara, CA, "Dynamics of an Earthquake Fault." (Division Sponsor: W.R. Kelly)

October 16, 1990

Anne P. Thorne, Department of Physics, Blackett Laboratory, Imperial College of Science and Technology, London, England, "Fourier Transform Atomic Spectroscopy in the Ultraviolet." (Division Sponsor: J.C. Travis)

November 3, 1990

G.P. Westphal, Atominstitut der Osterreichischen Universifaten, Schuttelstr. 115, A-1020 Vienna, Austria, "High Count Rate Gamma Spectroscopy." (Division Sponsor: R. Zeisler)

November 5, 1990

Brent J. Heuser, University of Michigan, Ann Arbor, Michigan, "Small Angle Neutron Scattering Measurement of Deuterium Trapping at Dislocations and Grain Boundaries in Palladium." (Division Sponsor: R.R. Greenberg)

November 9, 1990

Pavel Mader, University of Agriculture, Faculty of Agronomy, Prague, Czechoslovakia, "Dry Ashing and Its Chances in Trace Element Analysis." (Division Sponsor: G.C. Turk)

November 28, 1990

Peter C. Jurs, Department of Chemistry, Pennsylvania State University, Pennsylvania, "Prediction of Physical and Spectral Properties of Organic Compounds by Computer-Assisted Methods." (Division Sponsor: G.W. Kramer)

December 6, 1990

Ryszard Chojnacki, Hewlett-Packard Co., P.O. Box 301, MSC U308, Loveland, CO 80539, "Standard Commands for Programmable Instrumentation and the SCPI Consortium." (Division Sponsor: G.W. Kramer)

December 14, 1990

P.B. Farnsworth, Department of Chemistry, Brigham Young University, Provo, UT 84602, "Tweaking Atoms With Lasers." (Division Sponsor: G.C. Turk)

January 17, 1991

K. Aslihan Yener, Conservation Analytical Laboratory, Smithsonian Institution, Washington, DC 20560, "The Search for High Technology Metals of Antiquity." (Division Sponsor: R.D. Vocke)

February 5, 1991

Alexander Scheeline, National Science Foundation, Washington, DC, "Oscillating Reactions and Chemical Analysis." (Division Sponsor: G.C. Turk)

March 21, 1991

J. Michael Griesmeyer, Sandia National Laboratories, "The DoE Laboratory Automation Project." (Division Sponsor: G.W. Kramer)

April 3, 1991

Dr. Jeffrey Ryan, Carnegie Institute of Washington, Department of Terrestrial Magnetism, Washington, DC 20015, "The Systems of Boron (and ^{10}Be) and the Geology of Subduction Zones." (Division Sponsor: R.D. Vocke)

April 17, 1991

Muridan Kumakhov, Moscow, USSR, "New Neutron Optics with Wide Angular Aperture." (Division Sponsor: D.F.R. Mildner)

April 18, 1991

Ronald R. Williams, Department of Chemistry, Clemson University, "Signal-to-Noise Ratio: Warts and All." (Division Sponsor: M.R. Winchester)

May 15, 1991

Douglas Strong, Department of Chemistry, Texas Tech University, Lubbock, Texas, "Electrodialytic Eluent Generation and Suppression. Ultralow Background Conductance Suppressed Anion Chromatography." (Division Sponsor: W.F. Koch)

May 28, 1991

Svein Ivar Sagatun, Norwegian Institute of Technology, Division of Engineering Cybernetics, Norway, "The Norwegian Experimental Remotely Operated Vehicle." (Division Sponsor: G.W. Kramer)

June 25, 1991

Scott Tilden, Digital Equipment Corporation, "Instrument Interfacing--A Futuristic Vision." (Division Sponsor: G.W. Kramer)

July 19, 1991

Douglas Duckworth, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, "Overcoming Limitations In Glow Discharge Mass Spectrometry." (Division Sponsor: R.D. Vocke)

July 24, 1991

Dr. Leo W. Hollberg, Time and Frequency Division, NIST, Boulder, Colorado, "Introduction to Diode Lasers in Spectroscopic Applications." (Division Sponsor: G.C. Turk)

August 15, 1991

Dr. Rick Paul, Department of Chemistry, San Jose State University, San Jose, California 95192-0101, "Neutron Activation Analysis of Eucrite, Diogenite, and Howardite Meteorites: Antarctic vs Non-Antarctic Comparison." (Division Sponsor: R.M. Lindstrom)

August 29, 1991

Peter de B. Harrington, Department of Chemistry, Ohio University, "Minimal Neural Networks." (Division Sponsor: M. Salit)

September 12, 1991

Jack Harrington, Hewlett-Packard Co., "Healthcare Open Systems Communications." (Division Sponsor: G.W. Kramer)

c. Conferences/Workshops Sponsored/Co-Sponsored

October 6-7, 1990

IUPAC Commission on Isotope Measurements as References, National Institute of Standards and Technology, Gaithersburg, Maryland

October 31, 1990

CAALS Supercritical Fluid Extraction Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

November 1-2, 1990

CAALS Oversight Board Meeting, National Institute of Standards and Technology, Gaithersburg, Maryland

December 6-7, 1990

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

March 21-22, 1991

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

April 19, 1991

CAALS Spring Informational Meeting, National Institute of Standards and Technology, Gaithersburg, Maryland

June 25-26, 1991

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

September 12-13, 1991

CAALS Modularity Workshop, National Institute of Standards and Technology, Gaithersburg, Maryland

September 27, 1991

CAALS Fall Informational Meeting, National Institute of Standards and Technology, Gaithersburg, Maryland

d. **SRM Activities**

1084a wear metals in oil
1085a wear metals in oil
113a ore concentrates
122i cast iron car wheel
1271 stainless steel
1295 stainless steel
1296 stainless steel
1297 stainless steel
131e low carbon silicon steel
136e potassium dichromate
1400 bone ash
1486 bone meal
1515 apple leaves
1547 apple leaves
1573a tomato leaves
1619a fuel oil
1621d fuel oil
1622d fuel oil
1643c trace elements in water
186e phosphate pH buffer, equimol
186e phosphate pH buffer, physiol. 37
1930 glass filters (extended transmittance)
2031 metal-on-quartz filters (transmittance)
2034 holmium oxide solution (wavelength)
2171 stainless steel
2171a stainless steel
2183 pH buffer, mopso/mopsoate
2193 pH buffer, calcium oxide
2682a coal
2685a coal
2694a rainwater level I
2694a rainwater level II
2708 thin film standard
2708 coated filters
2709 soils
2710 soils
2711 soils
3101 spectrometric solution

3102 spectrometric solution
3103 spectrometric solution
3105 spectrometric solution
3106 spectrometric solution
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3168 spectrometric solution
3169 spectrometric solution
3171 spectrometric solution
3181 anion solution, sulfate
3181a anion solution, sulfate
3182 anion solution, chloride
3183 anion solution, fluoride
3184 anion solution, bromide
3185 anion solution, nitrate
3186 anion solution, phosphate
3191 electrolytic conductivity
3192 electrolytic conductivity
3193 electrolytic conductivity
329 ore concentrates
332 copper ore
8400 sewage sludge
893 stainless steel
895 stainless steel
909a human serum, level I
909a human serum, level II
919a sodium chloride
930d glass filters (transmittance)
955a bovine blood, level I
955a bovine blood, level II
955a bovine blood, level III
955a bovine blood, level IV
955a bovine serum, level I
955a bovine serum, level II
955a bovine serum, level IV

ORGANIC ANALYTICAL
RESEARCH

V. Organic Analytical Research Division (835)

Willie E. May, Chief

A. Division Overview

The Organic Analytical Research Division is the National source for measurement science and related information pertaining to the characterization and quantitative analysis of organic compounds in both simple and complex matrices, and the quantitative analysis of gaseous chemical species in air. The Division has a staff of 40 scientists and a annual budget of $5.1M.

The Division's mission is to conceptualize, develop and apply trace organic analytical and gas metrological methods and concepts to problems of scientific, industrial, and national concern. Research efforts are carried out in four groups: Analytical Sensors and Automation; Separation Science; Mass Spectrometry; and Gas Metrology Research. Research activities involving Division personnel resulted in 40 articles being published or in press in technical media during the past year. Division scientists presented 51 talks at scientific meetings and conferences during the past year; more than 50% invited.

The overall research program within the Division has four primary components: fundamental research and measurement activities in trace organic analytical chemistry and gas metrology (41%); research and measurement activities conducted in support of other Federal Agency programs on a reimbursable basis (37%); research and measurement activities in support of the NIST Standard Reference Materials Program (13%); research and measurement undertaken on a reimbursable basis from American Industry (9%). Research and measurement efforts within the Division led to the certification of 26 SRMs in FY91; 24 more are in progress, with completion expected early in FY92.

There has been rapid growth in organic analytical chemistry over the past decade. Organic analytical chemistry, and trace organic analysis in particular, is widely regarded as a "frontier" area in which major technological breakthroughs will continue to occur. Rapid growth in this area has been largely due to the development of new analytical instrumentation, techniques and procedures with improved sensitivity and specificity. Scientists in the Division are making significant contributions to the development, theoretical understanding and application of new and emerging chemical measurement technologies such as analytical sensors, capillary electrophoresis, and supercritical fluid extraction. Congressional Base and Competence support are used for the development and maintenance of these new and other core measurement technologies vital to providing trace organic and vapor phase standards and measurement support to our customer base, and for addressing the Under Secretary's goal world leadership in standards and measurement science.

Other Federal Government and State Agencies continue to comprise the Division's primary customer base, although interactions with, and support from, the Industrial sector has grown over the past few years. During the past year we were involved in 25 projects from 12 Federal and

State Agencies. The two largest Other Agency programs are related to providing analytical measurement quality assurance support for (1) epidemiological studies and cancer chemoprevention trials conducted by the National Cancer Institute (NCI) and (2) the National Status and Trends marine monitoring program being undertaken by NOAA. More than 65 laboratories worldwide involved in studies to investigate the cancer prevention efficacy of selected fat-soluble vitamins and other phytochemicals participate in the NCI QA program. NIST research and service activities have fostered a five-fold improvement in interlaboratory precision among the participants. We also serve as the analytical reference laboratory for approximately 30 investigators involved with the measurement of PAH, PCBs and chlorinated pesticides in marine sediments and tissues.

The majority of our research-related interactions with industry have come through our involvement with on two Consortia and two professional/trade organizations. The Consortium on Automated Analytical Systems (CAALS) is headquartered at NIST and has eleven U.S. based corporations and two Federal Agencies as members. Research efforts within the consortium are focussed on the production of U. S. industry-wide compatible systems for chemical analysis. As a direct result of our involvement with CAALS, we anticipate increased research involvement with several U.S. manufacturers of analytical instrumentation and a specialty gas company concerning supercritical and volatile liquid fluid extraction technology. The Biotechnology Research and Development Corporation (BRDC) is a consortium of seven biotechnology companies with facilities in the state of Illinois. Our collaboration with the BRDC involves the design, fabrication and evaluation of planar and fiber-optic waveguide phase-sensitive analytical sensors. The College of American Pathologists (CAP) is a professional organization of over 1000 physicians who specialize in pathology. The CAP oversees the performance of clinical laboratories in the U. S. through a variety of activities, including the administration of proficiency testing surveys. CAP-sponsored Research Associates apply NIST definitive methods technology to value assign many of the "unknown" pools and reference materials used in CAP programs. The Motor Vehicle Manufacturers Association (MVMA) is a trade association comprised of seven auto makers with manufacturing facilities in the U.S. Our current interaction with the MVMA involves the development and issuance of SRMs for measuring gaseous emissions needed to assist automotive industry compliance with 1990 amendments to the "Clean Air Act."

Research activities within the Division crosscut four of the six CSTL strategic thrust areas: Chemical and Physical Characterization, Laboratory Automation and Expert Systems, Sensors and Instrumentation and Separation Science. The Group Overviews and Technical Highlights that follow provide descriptions and discussions of specific research activities that emanate from the CSTL strategic thrust areas mentioned above and reflect the high quality and broad impact of the Division's research programs.

The Analytical Sensors and Automation Group was formed upon the establishment of CSTL from the remnant of the Division's Analytical Sensors Group, one new hire, and key staff from elsewhere in the Division. The Group's research activities encompass four general areas: (1) refinement, critical evaluation and application of Flow Injection Immunoassay (FIIA) technology; (2) development and application of optical planar waveguide sensors; (3) automation and refinement of trace organic measurement methodologies, including supercritical fluid extraction; (4) capillary electrophoretic separation of neutral organic and biomolecules.

FIIA is a measurement technology developed at NIST as part of a "Biosensors Competence Building Effort". The program began in 1986 and yielded a prototype device in FY90 that was field tested at NIH for the determination of theophylline in blood serum samples. Results for theophylline were comparable to a commercial analyzer. However, in the FIIA system, antibodies are reusable up to 400 times and only 0.2 vs 50 µL serum were required. In this system, Liposomes, phospholipid vesicles whose aqueous cavity can encase tens of thousands of marker molecules, are used to amplify immunochemical binding events rather than radioactive labels (RIA) or enzyme links (ELISA). During the past year we have worked with Anne Plant of the Biotechnology Division to initiate a FIIA project directed toward the determination of Lp(a)-cholesterol in serum. Lp(a) is the component of the low density lipoprotein (LDL) cholesterol thought to be related to genetic predisposition for coronary heart disease. There are currently no routine clinical assays for this analyte. During the coming year, we also plan to apply FIIA to the determination of estrogen steroid hormones being used as intermediate endpoint markers for breast cancer.

During FY91, considerable progress was made in our program for development of planar waveguide sensors. In these sensors, the evanescent wave of laser light propagating through planar waveguides interacts with an immobilized analytical reagent, generating an analytical signal. As a proof of principle, a sensor for theophylline that consisted of theophylline antibody immobilized on a silver ion diffused glass waveguide was developed and critically evaluated. A manuscript on this work, "Liposome-Enhanced Planar Waveguide Optical Immunosensors", has been accepted for publication in Analytical Chemistry. Through a collaborative effort with the Ionizing Radiation Division (Physics Laboratory), we are developing optical sensors for low-level radiation detection for use in quality control of polymer curing technologies and in- vivo chemotherapy.

During the past year a project was begun to develop and evaluate a laboratory robotics system for the extraction and HPLC analysis of retinol, α-tocopherol and β-carotene from human serum under the umbrella of our general reference laboratory-quality assurance role for NCI cancer chemoprevention studies. The poor quality of data from laboratories with high technician turnover prompted us to begin examining the practicality of robotic automation. However, use of the robot also provides a unique opportunity to research the variance associated with each step involved in the NIST, as well as other serum extraction procedures. To this end a collaborative effort has begun with Dave Duewer (837) on chemometric evaluation of the fat-soluble vitamin in serum extraction methodologies being used in various laboratories.

Significant progress was also made in [1] the development of capillary electrophoresis (CE) techniques for the separation and detection of neutral organic and biomolecules and [2] development of an automated supercritical fluid extraction and analysis module. The separation of DNA fragments, important to the biomedical and forensic communities, was accomplished in CE by the use of a soluble size-exclusion agent. A second project on the Micellar Electrokinetic

CE detection of gunshot and explosive residues also progressed greatly in FY '91. Several clay minerals were used as model matrices for arriving at robust supercritical CO_2 conditions for extraction petroleum hydrocarbons from soils. This is expected to become a very high volume analytical test as concerns increase about leakage of underground gasoline and diesel fuel storage tanks. As part of our involvement with the CAALS consortium, Code has been written to allow totally automated operation of a prototype "SFE-autosampler-GC-data acquisition and processing" system for conducting such analyses.

The Separation Science Group represents a synthesis of the Division's former Gas Chromatography and Liquid Chromatography Groups. Research activities in this Group are directed toward providing a unified and coordinated approach for (1) investigating the physical and chemical processes that influence chromatographic separation processes and (2) the development and use of chromatographic systems, including tailored stationary phases, for the separation, detection, and quantification of individual organic species in both simple and complex mixtures.

During the past year research efforts in the Group continued to address the molecular interactions that occur during chromatographic separations, most notably on shape selectivity investigations: charge transfer phases in LC and liquid crystalline stationary phases in GC. In the LC investigations, charge transfer phases were observed to discriminate between planar and nonplanar polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) thereby providing a means of isolating selected isomers. As part of our efforts in GC stationary phase research, we initiated a collaboration with a manufacturer of liquid crystalline GC phases directed toward identifying a set of molecular probe molecules whose elution characteristics will provide figures of merit for predicting the selectivity of that phase for separations of various classes of isomeric compounds.

The Separation Science Group is heavily involved in the application of gas and liquid chromatographic procedures to the determination of trace-level analytes in a variety of sample matrices as part of the NIST SRM program. The Separation Science Group has contributed to the development of 18 SRMs during the past year including: instrument calibration solution SRM's for amino acids, chlorinated pesticides, PAH and PCBs; pure carotenoid and chlorinated pesticide primary reference compounds; a fat-soluble vitamins in serum material; 3-drugs of abuse in urine materials; and 2-low ppm moisture in oil materials.

The Group continues to be involved in a number of measurement activities in support of other Federal Agency programs (EPA, NOAA, NCI, DoD). During the past year, a great deal of effort was devoted toward improving our capabilities for providing quantitative determinations of individual polychlorinated biphenyl (PCB) congeners in environmental samples by implementing two totally independent sample analysis procedures. This improved capability was used in support of EPA and NOAA programs and also for providing additional data on several NIST SRMs.

The Group is also involved in a continuing, long-term activity known as the National Biomonitoring Specimen Bank which involves the collection, storage, and analysis of a variety of environmental and biological specimens. Analyses of selected specimens for the determination of PCBs and pesticides have been performed to provide baseline data, assess the long-term storage stability of biological specimens, and provide a pool of samples for future retrospective analyses.

The Mass Spectrometry Group was virtually unaffected by the reorganization. Research efforts within the Group are focussed primarily on the development and application of mass spectrometric methodologies for the qualitative and quantitative trace organic analysis of complex mixtures. Particular emphasis is directed toward investigating the quantitative potential of mass spectrometry/mass spectrometry (MS/MS) and thermospray liquid chromatography/mass spectrometry.

During the past year, in an effort to improve our capabilities for characterization of biomolecules, MS/MS was applied to the structural characterization of pyoverdine, a peptide with some unusual amino acid residues, whose structure had been previously confirmed by NMR and FAB-MS. With FAB/MS/MS, ions observed previously using FAB/MS were observed with improved intensities, and additional structurally significant ions were present in the spectrum. Most important though, was a great reduction in extraneous, uninterpretable ions which most likely came from the matrix and from secondary fragmentations. For quantitative analysis, MS/MS was used to prove data used in the certification of drugs of abuse in complex matrices such as urine and hair.

The major focus of the group's SRM activities continues to be development of drugs of abuse in urine materials. Two new opiate in urine SRMs were certified in FY91. A new research activity within this Group involves investigating analytical aspects of the use of human hair for drugs of abuse, a promising alternative for urine drug testing. Analysis of hair provides certain advantages over urine analysis, but a number of analytical and other issues such as external contamination and effects of hair treatments are yet to be resolved and were a large component of NIST research efforts. NIST measurements for value assignment of a drugs of abuse in hair reference material have been completed. This materials should be available for purchase by the end of calendar year 1991.

Definitive method measurements were completed for two levels of urea in SRM 909a, Lyophilized Human Serum, in the past year. The five organic analytes for which definitive methods are available have all been certified in this SRM. The stability of the certified analytes were also investigated by remeasuring SRM 909, the predecessor to SRM 909a. During the coming year, plans are to apply the definitive method for total serum cholesterol to the determination of the cholesterol associated with the high-density and low density lipoprotein fractions of an SRM serum pool. Lp(a) measurements will be made by the Analytical Sensors and Automation Group.

The Gas Metrology Research Group came to the Division from the Gas and Particulate Science Division (Center for Analytical Chemistry) upon the formation of CSTL. The Group conducts research directed toward the development and measurement of primary gas standards. The knowledge and standards derived from these studies are applied to the quantitative evaluation of gas mixtures ranging in concentration from the percent to the parts-per-trillion (pptr) level, and in complexity from single to multicomponent gas mixtures. While the metrological outputs of the Group are focused on the certification of a wide variety of gaseous inorganic and organic Standard Reference Materials, a substantial portion of the Group's activities involves measurement research covering a very broad range of gas analyses. The gaseous reference materials developed by the Group serve as primary calibrants for both national and state regulatory programs and are widely used in U. S. industry. These reference materials are also used as accuracy benchmarks by many international standards organizations and are used in several global monitoring programs.

One of the new challenges for this Group is concerned with the development of "High Purity" gas standards. There is no particular characteristic of a gas that can be measured to infer it's absolute purity. Purity is determined by measuring the levels of the impurities for establishing total level of impurity, from which "purity" can be inferred. The Kennedy Space Center is one of our primary clients in need of high purity gases. Their particular interest is He in N_2 for use in calibrating instrumentation for detecting trace leaks around the space shuttle launch pad prior to and during launch. They require that the N_2 used be 99.9995% pure and that He be detectable at the 200 ppb level. Techniques with greater sensitivity and selectivity than those currently available are needed to substantially improve the state-of-the art in this area.

Recent amendments to the Clean Air Act have also been responsible for the direction of some of our research in regard to three gaseous species; methanol, formaldehyde and nitric oxide. Some portions of the recent amendments require that clean fuel be used in automobiles and the fuel is almost certainly going to be a mixture of gasoline and methanol. Because of this, there will be a need to set emission requirements for both methanol and formaldehyde. Methanol would be released by evaporative losses and unburned fuel. Formaldehyde would be released as a product of methanol combustion. The new amendments also stipulate that the level of NO in auto exhaust be reduced and that NO be determined more accurately. The Motor Vehicles Manufacturers Association has requested that NIST provide the calibration standards needed for the measurements required and have provided partial support for this endeavor.

B. Selected Technical Reports (Organic Analytical Research Division)

1. Radiation Dosimetry Using Planar Waveguide Sensors

S.J. Choquette, L.L. Brown, and M. Walker (PL)

Quality control of any technology using ionizing radiation, such as polymer curing or in vivo radiation therapy, suffers from the lack of accurate information on absorbed dose. The Analytical Sensors and Automation group (835) and the Radiation Interactions and Dosimetry group (846) have begun a joint effort to develop optical waveguide radiation dosimeters. The goal of this effort is to develop sensors for applications which require a real-time response to low levels of ionizing radiation. Currently, planar waveguide sensors using radiation sensitive coatings are under evaluation for these applications.

A planar waveguide is a thin (1-100 micron) dielectric film supported upon a rigid substrate. When the refractive index of the film is greater than the substrate and superstrate (typically air), light can be guided exclusively within the thin film by total internal reflection (TIR). Candidate polymer films that provide radiation sensitivity do not significantly attenuate this guided beam, and thus optical pathlengths of several centimeters are easily achieved.

In our approach to the development of these sensors, radiation sensitive dyes are incorporated into the thin polymer film waveguide. When the waveguide is irradiated with ionizing radiation, the dye becomes colored and absorbs the guided beam. The extent of light attenuation can then be measured and related to the absorbed dose of radiation. Because the optical pathlength parallel to the film is between 10 and 1000 times greater than the film thickness, optical attenuation measurements using the waveguide approach are expected to be significantly more sensitive than the currently used transmission measurements.

Three radiation sensitive media are currently under investigation for sensor development: Pararosaniline dyes, GaFChromic Radiation Dosimetry Media, and diffused silver ion waveguides. Pararosaniline dyes have been used extensively in commercial radiation dosimeters with UV-VIS detection. These dyes are readily dissolved in a number of polymers and can be spin coated onto glass substrates. The GaFChromic Dosimetry Media is a colorless, proprietary coating that also becomes colored when irradiated. This is obtained commercially as a 6 micron thick coating on a 100 micron mylar substrate. Light can be guided in this sandwich by TIR. In addition, waveguides fabricated by silver ion diffusion are under investigation. Silver ions exposed to ionizing radiation are reduced and form color centers which absorb visible light.

Filtered 100 keV X-rays were used as a model radiation source to compare the attenuation response of these waveguide sensors. In all cases, a 2 cm section of the waveguide was exposed to the X-ray source. Both the Ag+ and GaFChromic Media showed a linear response to doses between 1-100 gray (10-1000 rad). The pararosaniline dye film waveguides exhibited a dose response, but were very unstable. Preliminary results indicate however, that all three waveguides demonstrate an increase in sensitivity over conventional dosimetry media using UV-VIS detection. Future work will focus on the selection of the optimal sensitizing agent and optical design for radiation sensing.

2. Automation of Sample Preparation of Human Serum for the Analysis of Retinol, α-Tocopherol and β-Carotene Using Laboratory Robotics

S.N. Chesler, J.M. Brown Thomas, E. Schönberger (Guest Scientist), and D. Duewer (837)

Sample preparation for serum measurements is a time consuming and costly part of clinical analysis, often fraught with operator-dependant errors. NIST is investigating the use of laboratory robotics as a means of automating this crucial analysis step as part of a QA Program for 65 labs - worldwide, involved in cancer chemoprevention studies. As a test case, we are automating the procedure for the solvent extraction of the fat-soluble vitamins - retinol, α-tocopherol and β-carotene from human serum. The goal is to evaluate the accuracy, precision and sample throughput of this robotic sample preparation approach.

A commercially available, radial arm robot system has been assembled for serum extraction. In addition to the vendor-supplied sample tube racks and stations designed for dispensing, vortex mixing, evaporation and capping, a custom disposal apparatus and cap storage rack have been fabricated in-house for use in this project. The cap-storage rack allows us to uncap six samples and store the caps for later retrieval. In this manner tubes can be concurrently placed into the evaporator, subsequently removed and recapped. The custom disposal apparatus safely stores potentially bio-hazardous expendables (tubes and pipet tips). A balance station has also been added, even though it will not be used in routine extraction procedures. Instead, it is being used to monitor and optimize the quantitative liquid dispensers (syringe hand, automated pipets, and cannula).

An important component of the robotic system is the design and testing of the controller software. Robot motions are controlled through a series of instructions contained within BASIC programs. In order to optimize the robot for sera analysis, many of the vendor-supplied programs had to be modified. Customized software has also been written to control the robotic actions with the NIST-built hardware and to simultaneously operate more than one hardware module at a time.

In addition to our goal of implementing the serum extraction, we are in the process of conducting a number of chemometrically-designed experiments to investigate each step of the procedure. Because of the exquisite level of control and reproducibility of operations, the robot is a powerful tool for such repetitive measurements. We hope to unambiguously describe the variances associated with the individual sub-processes in the serum extraction and compare those to the variance associated with the final LC measurement. One particular challenge is to evaluate

3. CE Separation of DNA Fragments Using Soluble Size-Exclusion Agents and Deactivated Capillaries

W.A. MacCrehan and H. Rasmussen

The separation and identification of DNA fragments, cleaved by restriction enzyme endonucleases, has become the cornerstone for many critical measurements in molecular biology. The current technology for the separation of DNA relies on slab-gel electrophoresis, a technique which requires 3 days for sample preparation, separation, radiolabel detection and gel scanning. With the coming importance of DNA fragment analysis to the Human Genome Initiative and to forensic identification, a more rapid approach is needed.

During the past year, we have developed and evaluated a capillary electrophoresis approach using a soluble polymer size-exclusion agent for DNA fragment measurement. The system uses a coated silica capillary, chemically derivatised with a linear polyacrylamide layer using a silane linkage. The coating is necessary to eliminate the electroosmotic flow normally found in silica capillaries and also to prevent adsorption of the DNA to the capillary walls. A test of the longevity of this coating for use in the pH 8 separation buffer showed efficacy for 35 to 50 electrophoretic runs before failure.

Since DNA fragments have a constant ratio of charge to size, techniques used for their separation require a means for discrimination based on size. Although the development of solid gels for use in capillary electrophoresis has been published in the scientific literature, this approach has proven cumbersome in practice because of difficulty in fabricating robust and reproducible gels. Our approach uses a soluble "gel" agent, methylcellulose, to discriminate between the different sized DNA fragments. By optimizing the agent concentration and electric field strength, all 23 components of the standard DNA fragment mixture "1KB ladder" can be baseline resolved in under 25 minutes. This paves the way for more rapid fragment analysis using the CE technique. However, future work will be required to optimize the sample preparation for specific DNA fragment samples such as those generated by the polymerase chain reaction (PCR) amplification technique. Current limitations of our technique for such applications include the need to increase capillary coating longevity, lack of sensitivity of the direct, short pathlength ultraviolet detection and the need to remove Mg^{+2} and other salts prior to analysis. Dennis Reeder and Kannen Srinivasan of the Biotechnology Division (831) have taken this technology and are tackling the practical obstacles associated with day-to-day use of this new procedure.

4. Sampling Microparticulate Gunshot Residues Using Micellar Electrokinetic Capillary Electrophoresis (MECE)

D.N. Northrop (Guest Scientist) and W.A. MacCrehan

The alarming increase in violent crime in the U.S. has sparked the effort to develop new forensic technologies. One technique that seems particularly well suited to this challenge is capillary electrophoresis (CE). The physical dimensions of the required apparatus make possible the characterization of the limited quantity of sample found as evidence. In this project, we have worked with the National Institute of Justice in evaluating CE technology for the forensic identification of post-firing residues from firearms and explosives.

The CE technique utilizes small (50 to 100 μm) fused silica capillaries filled with dilute buffer. Application of a electric field provides separations based on analyte size and charge differences. In order to separate neutral molecules found in gunpowders and explosives, charged micellar agents, such as sodium dodecylsulfate (SDS), are added to the electrolyte to provide a nonpolar pseudo stationary phase. In this Micellar Electrokinetic CE (MECE) procedure, neutral analytes distribute between the buffer and the micelles based on their hydrophobicity, much as in reversed phase LC. The difference between the velocity of the micelles and the bulk electrolyte flow (electroosmotic flow) causes a difference in net migration, thereby separating the compounds. On-capillary UV/visible absorbance detection completes the measurement.

Currently, the analysis of gunshot residues is most commonly done by atomic absorption spectrometry and scanning electron microscopy; both techniques being used to detect minute traces of inorganic primer residues. Both techniques are expensive to use, and require considerable operator skill. These factors have limited the use of residue analysis to less than 1% of the possible criminal investigations. We have developed a MECE technique that focuses on the organic constituents, which comprise the bulk of gunpowder and explosive formulations. The MECE system can separate 27 constituents of gunshot or explosive residues in 15 minutes, with detection limits on the order of about 10 picomoles. We have found that the pattern of occurrence of the organic propellants and stabilizers in gunpowders and explosives varies with the manufacturer and lot. After firing, this recognizable pattern remains, allowing identification of the source.

In FY91, much attention was directed toward improving the qualitative and quantitative results achieved by MECE. We have indexed all migration times to two components, one of which is completely retained by the micelles and one other unretained. This reduces the migration time variability from 10% to 0.5%. Indexing quantitation to an internal standard has improved peak area reproducibility from about 20% to 5%.

Currently, we are focusing our attention on the sample collection and processing technique. A masking tape film lift has been shown to provide excellent sample recovery for particles of burned, semi-burned and unburned gunpowder deposited on the weapon-firing hand. A single particle (of less than 0.1 μg) can be microscopically isolated and extracted for analysis by MECE.

Identifiable signals from these tape lifts can be obtained under the appropriate extraction conditions. Further studies will be aimed at establishing a database for gunpowders and explosives from different manufacturers, and for different lots from the same manufacturer.

5. Supercritical Fluid Extraction of Diesel Fuel from Clay and Soil Matrices

S.N. Chesler, A.P. Emery, and W.A. MacCrehan

About 18 months ago, the Consortium on Automated Analytical Laboratory Systems (CAALS) was formed with the objective of developing U.S. industry-wide compatible systems for chemical analysis. The consortium is headquartered at NIST and has eleven private sector organizations and Federal Agencies as members. In order to support the CAALS effort, the Organic Analytical Research Division has initiated a program to investigate new technologies suitable for automated organic analysis. In FY91, the CAALS organic project has focused on evaluating the suitability of Supercritical Fluid Extraction (SFE) for the automation of the sample preparation process. Our initial target is to provide a technique for the automated SFE of soil contaminated with diesel fuel.

The measurement of contamination resulting from leaking diesel oil storage tanks and surface fuel spills is a continuing national environmental concern. Currently, determination of the diesel content of contaminated soil relies on two EPA-accepted sample preparation methods: Soxhlet extraction and ultrasonic solvent extraction. However, these methods have several inherent drawbacks: large volumes of hazardous organic solvents must be used and subsequently disposed of; careful technical manipulation is required to obtain accurate results; and Soxhlet extraction requires considerable time. We are investigating a new approach to the analytical extraction of diesel contaminants from soil using supercritical fluid extraction (SFE). Instead of organic solvents, SFE uses only small amounts of relatively inert gases, compressed and heated above the critical point. Following the sample extraction process, the pressure is released and the extract can be deposited as a concentrate either in a liquid solution or onto a column packed with a chromatographic stationary phase. In addition, since the solvation properties of the extractant can be manipulated readily by temperature and pressure during the extraction period, conditions can be adjusted to make SFE more selective than currently solvent extraction techniques. SFE also shows great promise to become a fully automated process, lowering analysis time and costs.

A new method was developed for the quantitative extraction of diesel fuel oil from different clay and soil matrices using supercritical CO_2. Clays were studied because they represent one of the major adsorptive fractions of soils. In addition, because these clays are relatively well-characterized materials, they could be used as model matrices to investigate the details of the SFE recovery process.

Our research shows that conditions required for quantitative extraction are dependant on both the analyte and sample matrix. In general, diesel fuel oil was easier to quantitatively extract from the contaminated soils than from the clays. The large internal surface areas of the clays allowed greater sorption and retention of the diesel material. We found that high extraction densities improve the solvating power of the supercritical fluid, and high extraction temperatures improve analyte volatility and diffusivity; the combination of the two provides quantitative recovery. By determining the SFE conditions required for the comparatively difficult extraction of the diesel fuel from clay matrices, we are assured of developing a robust method suitable for analysis of the full range of U.S. soil types.

An interlaboratory comparison study and workshop were conducted to focus attention on the capability of SFE to address this national measurement problem. Two diesel fuel contaminated clays, a diesel fuel contaminated soil and a sediment sample contaminated with PAH and PCBs were used as test samples by 18 laboratories. At the workshop, scientists from the industrial community, academia and government laboratories presented their analytical results on this common set of samples and discussed various aspects of their SFE research. In general, there was agreement concerning the total aliphatic hydrocarbon content of all samples, demonstrating the feasibility of using SFE for these frequently performed analyses. We are beginning an effort to develop and demonstrate a fully automated analysis system for diesel hydrocarbons in soil. Software and hardware are being developed to pass the soil sample extracts from a commercial SFE extraction station to a GC or GC/MS system for separation and quantitation. The successful development of this interface will be the first key element in a fully automated system to address this problem of measuring diesel contaminated soil.

6. Retention Mechanisms in Liquid Chromatography Using Charge Transfer Phases

L.C. Sander, R.M. Parris, and S.A. Wise

A variety of factors affect the ability of a given column to discriminate between compounds on the basis of molecular shape (shape selectivity). In reversed-phase systems, bonded phases based on monomeric surface modification exhibit low shape selectivity; phases based on polymeric surface modifications exhibit enhanced shape selectivity. Even greater shape specificity is exhibited by charge transfer columns, operated in the normal-phase mode. Charge transfer phases usually consist of immobilized aromatic species that contain either a surplus or deficit of electron density. Polycyclic aromatic hydrocarbons (PAHs) are retained on electron acceptor phases (commonly based on nitrated or halogenated aromatic species), and polychlorinated biphenyls (PCBs) are retained on electron donor phases (e.g., a bonded pyrene ligand). We have studied the retention behavior of both PAH isomers and PCB congeners on electron acceptor and electron donor phases to ascertain the effect that solute shape may have on retention. By using isomer sets, variables that are known to strongly influence retention (such as aromatic carbon number) are held constant, and the influence of more subtle effects of solute shape can be directly evaluated.

The effect of solute shape was probed for electron acceptor charge transfer columns using three sets of PAH isomers (MW 278, 302, and 328). Structures for these isomers were determined using molecular modeling computer programs to determine the degree of nonplanarity in each molecule. Such programs have proven useful in previous studies for structure elucidation of nonplanar PAH molecules. For each of the isomer sets, nonplanar compounds were observed to elute before any of the planar compounds, and class separations based on molecular shape were possible. This retention behavior was observed for two electron acceptor charge transfer phases based on dissimilar bonded phase ligands (i.e., tetranitrofluoreniminopropyl and tetrachlorophthalimidopropyl groups). We hypothesize that the reduced chromatographic retention observed for nonplanar PAHs results from a weaker charge complex of the solute with the bonded electron acceptor ligand. Planar solutes, which are able to interact more fully with these bonded ligands, form stronger charge transfer complexes and are retained longer.

The retention behavior of a second class of compounds, polychlorinated biphenyls, was also studied using charge transfer columns. Because PCBs are highly chlorinated, an electron donor charge transfer phase based on an electron rich donor group (bonded pyrene) was utilized. PCB congeners vary in the position and number of chlorine substituents about the biphenyl rings. Among the most toxic PCBs are planar congeners with multiple chlorination at ring positions 3, 4, and 5. Chlorinated biphenyls for which no substitution is present at ortho positions (i.e., 2, 2', 6, or 6' positions) are classified as nonortho or planar (often denoted as "coplanar") PCBs, since planar conformations are permitted sterically. PCBs with two or more ortho chlorines are sterically constrained from the planar conformation; these compounds are referred to as nonplanar PCBs.

As with the PAH isomers, planar PCB congeners were retained longer than nonplanar congeners. This information is of practical significance since planar PCB congeners are typically more toxic than nonplanar PCBs, and measurement of levels of planar PCBs is complicated by the lower concentrations (10-100 times) of planar vs. nonplanar congeners and by the coelution of nonplanar and planar congeners on conventional gas chromatographic stationary phases. This charge transfer separation step is now being used as part of an analytical procedure for the determination of PCBs in complex environmental samples (e.g., mussel tissue and marine mammal blubber).

7. Measurement of Carotenoid Compounds in Serum and Food Matrices

N.E. Craft, J.M. Brown Thomas, and K.S. Epler

Carotenoids are red, orange, and yellow pigments which impart color to foods, plants, and animals. More than 600 carotenoid compounds have been identified in nature. Since the 1930's some of these compounds have been shown to possess vitamin A activity. More recently, carotenoids have been implicated in cancer prevention, bolstering the immune system, and resistance to coronary artery disease. Because of their labile nature and structural similarity, individual carotenoids are difficult to measure accurately. As a result of these analytical difficulties, the National Cancer Institute has supported research at NIST to improve the extraction, separation, and quantitative measurement of carotenoids in human serum and foods.

We have evaluated the separation and recovery of seven carotenoid standards which account for approximately 90% of carotenoids present in human serum using 65 different reversed-phase liquid chromatography columns. A number of factors were identified that influence the measurement of carotenoids. Most striking was the diminished recovery of carotenoids from more than 90% of the LC columns when acetonitrile-based solvents were used as eluents. We have found, as recently reported by others, that the incorporation of ammonium acetate in the mobile phase increases the recovery to nearly 100%. The mechanism responsible for this phenomena is still under investigation.

Additionally, we have determined that polymerically-synthesized C_{18} packing materials yield better separation of carotenoid isomers. The pore diameter of the column packing also influences the discrimination among structurally similar carotenoids. There appears to be a delicate combination of pore diameter, polymeric-synthesis, surface coverage, column temperature, and mobile phase composition which yields optimum recovery and separation of carotenoids. Investigations are underway to identify the optimum combination of these parameters. Column temperature is also a critical component of carotenoid separation and quantitation. Temperature influences carotenoid measurements in three ways: retention time reproducibility, relative retention (stationary phase selectivity), and carotenoid solubility. By thermostatting the column at any temperature between 20° and 40 °C, reproducible results will be obtained. The influence of temperature on solubility and selectivity are competing effects. The solubility of carotenoids and associated lipids is greater at elevated temperatures; however, the selectivity for separation of isomers is diminished. Thus, a compromise between maximum selectivity and complete solubility is required.

Using the results of these investigations, we have developed LC methods for the measurement of carotenoids and fat-soluble vitamins in serum and food matrices. The methods generally utilize a polymeric C_{18} stationary phase, biocompatible frits, ammonium acetate-buffered mobile phase, and a thermostatted column to optimize the selectivity, recovery, and reproducibility of carotenoid measurements. These methods have been implemented for the measurement of a number of carotenoids and fat-soluble vitamins in over 200 human serum samples from an NCI cervical cancer study; an additional 1000 samples from this study and several hundred samples from other NCI studies will also be analyzed using this methodology.

SRM 968, Fat Soluble Vitamins in Human Serum, was prepared in 1989 as a secondary standard for the determination of β-carotene, retinol and α-tocopherol in serum in support of NCI programs. Since the supply of SRM 968 has been depleted, a new serum material, SRM 968a, is being certified. In addition to the analytes measured previously in SRM 968, the new material will also have values for lutein, zeaxanthin, β-cryptoxanthin, lycopene, α-carotene, 9-cis-β-carotene, and 13-cis-β-carotene, thereby providing a reference material to assist a wider community of researchers. An SRM for fat-soluble vitamins and carotenoids in a mixed diet matrix is scheduled for preparation during 1992.

8. Analytical Method Developed to Investigate the Role of Vitamin C in Cancer Prevention and Juvenile Arthritis

S.A. Margolis

The role of vitamins with antioxidant properties in the prevention of certain classes of diseases such as cancer has come under closer scrutiny in recent years. In a collaborative project with the Division of Cancer Etiology at the National Cancer Institute, a method has been developed for the accurate and precise measurement of vitamin C in human plasma. In addition, methods were developed for stabilizing calibration standards and for preparing stable and homogeneous quality control materials (70 °C). Studies were conducted to assess the long-term stability of vitamin C in preserved frozen plasma and the short term stability in whole blood (4 °C). These studies demonstrated that plasma samples containing vitamin C can be stored for at least one year without measurable analyte degradation and that vitamin C remains intact for at least six hours in whole blood. These studies were also used to assess the performance of laboratories participating in NCI studies designed to examine the role of vitamin C in carcinogenesis.

In another collaborative study with the Washington Children's Hospital and George Washington University, the vitamin C blood serum content of patients with juvenile arthritis was measured. The serum vitamin C levels correlated well with the pathological types of arthritis exhibited by the patients. Each of these studies, the multi-laboratory study on relationship of vitamin C to cancer incidence and the grouping of pathological states as a function of serum vitamin C levels, requires the use of accurate and precise trace organic measurement technology.

9. NIST Expands QA Activities Related to Monitoring of the Marine Environment

R.M. Parris, R.E. Rebbert, M.M. Schantz, and S.A. Wise

The analytical quality assurance and reference laboratory activities conducted by the Organic Analytical Research Division, in support of marine pollution monitoring programs, have expanded both in terms of number of participating laboratories and programs represented. Initially funded by the National Oceanic and Atmospheric Administration (NOAA) in 1987 in support of its National Status and Trends (NS&T) Marine Monitoring Programs, this ongoing project now has 28 participating laboratories that are involved in determining key organic contaminants in bivalve, sediment, and fish samples from the marine environment. In addition to several NOAA laboratories, program participants include laboratories from the Environmental Protection Agency Environmental Monitoring & Assessment Program (EPA-EMAP), the State/Federal Natural Resource Damage Assessment Program (Valdez Oil Spill Damage Assessment), the Food and Drug Administration, and a number of state environmental and health agencies.

The primary goal of the NIST/NOAA Marine Monitoring Quality Assurance Program is to provide a means for evaluating the quality of the analytical data from these laboratories. Specifically, the NIST efforts are focused on assessing the interlaboratory and temporal comparability of data, and on improving measurements for the monitoring of contaminants such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), and chlorinated pesticides in the marine environment.

NIST activities within this program include conducting intercomparison exercises, developing reference and other control materials, developing improved analytical methods, providing technical assistance to the participating labs and program managers, and conducting an annual QA workshop. This program has also resulted in the development of nine new SRMs including calibration solutions for the analytes of interest and natural matrices such as sediment and mussel tissue.

The expansion of this analytical quality assurance program will have impact beyond assessing the quality of analytical data for the individual programs. Assessment of and improved multiagency comparability of analytical measurements will facilitate the interrelation of data from various monitoring programs for expanded use in decision-making processes.

10. Specimen Banking Activities Related to Marine Mammal Monitoring

S.A. Wise, B.J. Koster, M.M. Schantz, R. Demiralp (834), and E.A. Mackey (834)

The Pilot Environmental Specimen Bank project was established at NIST in 1979 in conjunction with the U. S. Environmental Protection Agency (EPA). Since that time, specimen banking activities at NIST have expanded to include a variety of specimens from several projects of national and international interest. The National Biomonitoring Specimen Bank (NBSB) at NIST now consists of four major projects supported by the EPA, the National Oceanic and Atmospheric Administration (NOAA), and the Minerals Management Service (MMS). The two most recent projects, the Alaska Marine Mammal Tissue Archival Project (AMMTAP) and the National Marine Mammal Tissue Bank (NMMTB), have focused on the collection, banking, and analysis of marine mammal tissues, and they are part of a comprehensive plan to address marine mammal monitoring, specimen banking, and quality assurance of analytical measurements associated with contaminant analyses in marine mammals.

The goal of the AMMTAP, established in 1987 with funding from MMS (Department of Interior), is to archive a representative collection of Alaskan marine mammal tissues for future contaminant analyses. The results of these analyses can be used to document long-term trends in environmental quality. In the past five years selected tissues (blubber, kidney, and liver) from 65 individual marine mammals (seven species) from seven different sites in Alaska have been included in the bank. In 1989 the Office of Protected Resources, National Marine Fisheries Service (NMFS) within NOAA initiated the development of a National Marine Mammal Tissue Bank patterned after the successful banking program for Alaskan marine mammals. The NMMTB is part of a comprehensive marine mammal program within NOAA that also includes stranding networks, contaminant level monitoring, and quality assurance of chemical analyses.

NIST is involved in both specimen banking and analytical measurement quality assurance activities associated with this comprehensive program.

In 1990 a demonstration project was established to evaluate the practical aspects of obtaining suitable specimens for the NMMTB from both incidental catches during commercial fishing and from mass strandings. The northeast U.S. was selected for implementation of the demonstration project based on the potential access to marine mammals from incidental catches and mass strandings and on the willingness of scientists at the New England Aquarium (Boston, MA) to assist in the collection. Two species of marine mammals were targeted for the demonstration phase: (1) harbor porpoises (*Phocoena phocoena*) from incidental catches, which represent a coastal species, and pilot whales (*Globicephala macrorhyncha*) from mass strandings, which represent a pelagic species. For the demonstration phase, blubber and liver were identified as the most appropriate tissues for specimen banking. During the past year, the logistics and procedures for obtaining samples from both incidental catches and mass strandings were evaluated during the collection of specimens from 10 harbor porpoises and from 10 pilot whales.

As part of the NOAA NMFS marine mammal program, analytical results for contaminants in marine mammal tissues will be generated by several laboratories in both the monitoring component and the NMMTB component. To provide accurate analytical data requires a quality assurance (QA) component to assess the accuracy and comparability of results among the various laboratories. A quality assurance component has been developed for both the organic and inorganic analyses by NIST in conjunction with the NMFS. This QA program consists of (1) interlaboratory comparison exercises among NIST and other laboratories involved in NOAA projects related to marine mammal tissue analyses; (2) preparation, analysis, and distribution of marine mammal tissue control materials; and (3) development of Standard Reference Materials (SRMs) for use in the analysis of marine mammal tissues. During the past year large batches of whale blubber and liver (2 kg each) have been prepared as analytical control materials for organic and inorganic analyses, respectively. These two control materials have been analyzed at NIST and distributed to other laboratories as an interlaboratory comparison exercise. Recently, approximately 25 kg of blubber was collected from a stranding of pilot whales on Cape Cod. This material will be used to prepare a standard reference material to assist in quality assurance of analytical measurements for the determination of polychlorinated biphenyls and chlorinated pesticides.

11. Determination of Polycyclic Aromatic Hydrocarbon in Combustion Samples: Markers for Source Identification

B.A. Benner, Jr., S.A. Wise, and W.E. May

The characterization of different combustion sources for polycyclic aromatic hydrocarbons (PAHs) remains an important endeavor in environmental chemistry, particularly when one considers the large number of different sources, as well as the continuous improvement in techniques for the separation and detection of individual PAH isomers. Toward this end, ten combustion-related samples from the U. S. Environmental Protection Agency and several environmental Standard Reference Materials (SRMs) were analyzed by gas chromatography with mass spectrometric detection for the determination of selected PAHs for use as markers of various combustion sources. The samples analyzed were representative of the following combustion sources: residential wood burning, automotive emissions, diesel exhaust, aluminum smelter emissions, roofing tar, coke oven emissions, polyethylene incineration emissions, and petroleum crude oil.

To obtain results for a large number of PAHs, two GC columns were used in this study: a conventional nonpolar 5% phenyl-substituted methylpolysiloxane phase (DB-5) and a smectic liquid crystalline stationary phase. The DB-5 column, which is the typical stationary phase used for PAH separations, was used to measure the majority of the PAHs including phenanthrene, anthracene, methylphenanthrenes and dimethylphenanthrenes. The liquid crystalline stationary phase provides enhanced separation of PAH isomers. For example, four isomers of molecular weight (MW) 228, seven isomer of MW 252, and seven isomers of MW 278 were completely resolved on the liquid crystalline column whereas many of these isomers coeluted on the DB-5 column.

Ratios of selected PAH have been shown to be indicative of the type of source, e.g,, combustion (pyrolytic) or geological (petrogenic). For example, a phenanthrene/anthracene (Phen/Anth) ratio of $< 20 - 50$ is indicative of pyrolytic sources, whereas values of this ratio greater than 50 indicate a petrogenic origin. All of the combustion source samples had low Phen/Anth values (about 3 to 20) except for an automotive diesel exhaust sample, which probably represents unburned fuel on the particles, and the petroleum crude oil sample. Two methylphenanthrene ratios have been used by other scientists to differentiate sources: MPI (ratio of sum of 2-methyl- and 3-methylphenanthrene to sum of 1-methyl-, 4-methyl-, and 9-methylphenanthrene isomers) and ΣMP/P (ratio of sum of all methylphenanthrene isomers to phenanthrene concentration). For values of MPI > 1.5 and ΣMPI/P < 1, the source is generally pyrolytic. The values for MPI and ΣMP/P for the different source samples analyzed were consistent with previous results except for the residential wood combustion sample, which had values of 0.9 (MPI) and 2.5 (ΣMP/P). The values for wood combustion are anomalous since the input of methylphenanthrenes from natural precursors present in wood alter these ratios. We have also found that the level of 1,7-dimethylphenanthrene (DMP) is directly related to input from wood combustion. For all of the samples analyzed, the ratio of 1,7-DMP/2,6-DMP was less than 1, except for two samples that were heavily impacted by residential wood combustion.

Since we determined several isomers that are not routinely measured, we examined several additional PAH ratios to determine their potential as source markers. The ratio of chrysene/triphenylene (MW 228) ranged from 3.2 to 7.4 for the different source samples with the two automotive diesel samples having the low ratio of 3.2, whereas this ratio for the other samples was consistently between 6 and 7. The ratio of dibenz[a,c]anthracene/dibenz[a,h]anthracene (MW 278) showed similar trends, with ratios near 0.7 for all except the diesel samples (ratio of 1.3). These two ratios for the diesel samples may be due to the enrichment of triphenylene and dibenz[a,c]anthracene in the unburned fuel that coats the diesel particulate matter. Another ratio of 278 MW isomers, picene/dibenz[a,h]anthracene, ranged from 1.0 to 5.9 but showed no correlation with previous source indicators.

The differences in relative concentrations of specific PAHs in these different combustion source samples suggest that source contributions to field samples may be resolvable and that selected PAH ratios may serve as indicators of various source inputs.

12. Investigations of the Applicability of MS/MS for the Determination of Peptide Structure

E. White V, S.Y. Wang (Guest Scientist), and D.K. Hancock (831)

Last year we determined the primary structure of pyoverdine, a fluorescent iron-chelating peptide isolated from *Pseudomonas fluorescens* 244 by a combination of amino acid analysis, ^{1}H and ^{13}C NMR, and fast atom bombardment (FAB) mass spectrometry. That structure was succinyl-chromophore-seryl-lysyl-β-hydroxyhistidyl-threonyl-seryl-cyclo-δN-hydroxyornithine, where the chromophore was the pyrimidoquinoline structure expected for a pyoverdine.

The mass spectrometry, done by positive ion FAB (Cs^+ bombardment) on a magnetic instrument, contributed to determining which amino acids were present, and provided the molecular weight, the number of nitrogen atoms present (from a fully ^{15}N-labeled pyoverdine), and the sequence. Since large amounts of material were available, sequence information was obtained from averaging many spectra of the pyoverdine, the fully ^{15}N-labeled pyoverdine, and from partial hydrolysis products. The sequence was therefore considered to be reliable, but many of the observed characteristic peptide ions were weak with extraneous ions of similar intensity nearby.

The availability of material, the known sequence, and the difficulty of extracting adequate information from simple FAB provided near ideal circumstances to test the capabilities of tandem mass spectrometry (MS/MS) using a triple quadrupole mass spectrometer for the determination of peptide structures. The protonated molecular ions of pyoverdine and ^{15}N-labeled pyoverdine generated by FAB (Cs^+ bombardment) were induced to fragment by collision with argon in the second quadrupole to give daughter ion spectra. The spectra were collected under conditions similar to those used by Hunt of the University of Virginia, and supported by the instrument manufacturer for peptide sequencing. Thus, the resolution of the first quadrupole was set for a window of 4-5 mass units. This increased the sensitivity, but, as a result, the masses of the daughter ions were uncertain to about ±1 mass unit. Ions seen by simple FAB on the magnetic instrument were observed at moderately improved relative intensities by MS/MS and a number of additional ions of structural significance were observed. Most important though was a great reduction in extraneous uninterpretable ions that most likely come from the matrix and from secondary fragmentations.

The simplicity of the MS/MS spectra makes interpretation easier and less subject to error, but, at the same time the uncertainty in the masses of the ions introduces a complication. For normal peptides, where the possible mass separations of sequence ions are limited by the possible number of amino acids, the mass uncertainty will only infrequently pose a problem. In the present case, however, four of the eight components are not standard amino acids, and their masses were not known with certainty until deduced from the FAB spectra obtained on the magnetic instrument. It is unlikely that the masses and sequence of the components could have been absolutely deduced from the MS/MS experiments.

MS/MS can be a useful tool for peptide structure determination in conjunction with other analytical techniques. It appears to be best suited for determinations of the sequence of normal peptides, where the uncertainties about the daughter ion masses are less of a problem.

13. Investigations of the Quantitative Potential of MS/MS

C.C. Allgood, L.T. Sniegoski, S. Tai (Research Associate), and M.J. Welch

Tandem mass spectrometry, often referred to as mass spectrometry/mass spectrometry or MS/MS, is widely used for structural determinations and kinetic studies. This technique involves using one mass spectrometer analyzer to select certain ions, allowing these ions (usually referred to as parent ions) to undergo collisions with neutral species, and then using another analyzer to determine the product ions (daughter ions) from these collisions. Because particular parent ion - daughter ion combinations can be very specific to a given compound, they can be used to positively establish the presence of that compound. These parent-daughter ion combinations produce signals that are much weaker and less stable than are observed for either ion individually. However, background signal levels are also considerably reduced.

We have been investigating the applicability of MS/MS techniques to quantitative determinations of analytes present at ppm and ppb levels in complex matrices. A triple quadrupole mass spectrometer, in which collisions take place in the middle quadrupole, has been used for these studies. Three scanning modes are possible with this type of instrument: daughter scans, for which the first quadrupole selects one mass/charge ratio to pass and the third quadrupole scans a mass range to determine the daughter ions formed; parent scans, for which the first quadrupole scans a mass range while the third quadrupole is set to pass only ions of selected mass/charge ratio; and neutral loss scans, for which both quadrupoles are scanned but at any given time are offset from one another by a constant mass/charge difference. The neutral loss approach, with the scans restricted to narrow ranges, has proven to be the most sensitive, and consequently, the most applicable for quantitation. Because of the complexity of optimizing the daughter ion detection, a large number of parameters must be carefully controlled.

To determine the quantitative potential of MS/MS, we have applied our approach to the quantitation of drugs of abuse in urine- and hair-based reference materials. Measurements using direct probe introduction of underivatized codeine and morphine extracted from a freeze-dried urine SRM, coupled with MS/MS, confirmed the accuracy of GC/MS and LC/MS determinations of these analytes in this material. Chemical ionization MS/MS measurements of cocaine and benzoylecgonine extracted from a hair powder reference material were in excellent agreement with GC/MS results on the same material. Measurement precision for MS/MS has been equal to that for GC/MS and the high specificity of MS/MS reduces the likelihood of measurement interference, particularly when coupled with gas chromatography. MS/MS may even be useful for quantifying drugs directly in powdered hair materials without an extraction step. Preliminary experiments demonstrated that signals from the drugs were easily distinguished from the background when powdered hair was directly introduced via a direct probe. However, hair segments produced ambiguous results. Results from these studies demonstrate that MS/MS is useful for quantitation of analytes at ppm and ppb levels in complex matrices.

14. Development of Measurement Methods and Standards for the Determination of Drugs of Abuse in Urine and Hair

C.C. Allgood, R.G. Christensen, P.M. Ellerbe (Research Associate), L.C. Sander, L.T. Sniegoski, S. Tai (Research Associate), and M.J. Welch

NIST has an on-going program, in cooperation with the College of American Pathologists, to develop urine-based Standard Reference Materials (SRMs) for drugs of abuse. These SRMs are intended for use as primary controls for evaluating the accuracy of routine laboratory methods. SRM 1507 and its replacement, SRM 1507a, contain certified concentrations of the principal urinary metabolite of marijuana. SRM 1508 contains certified concentrations of cocaine and one of its principal metabolites, benzoylecgonine. Certification measurements were completed in FY91 for two opiate in urine SRMs. The first, SRM 2381, consists of three levels each of free morphine and codeine. Methods that were developed for the certification included GC/MS, LC/MS, and direct probe MS/MS. The second, SRM 2382, consists of three levels of morphine glucuronide, the conjugated form that accounts for a large percentage of the morphine excreted in the urine. Certification involved two independent hydrolysis procedures to free morphine followed by analysis using the same GC/MS and LC/MS methods used for certifying morphine in SRM 2381.

Recently, considerable attention has focussed on the analysis of hair for detection of illegal drug use. Hair can be acquired without the privacy complications associated with collection of urine specimens and is thought to provide a long-term record of drug use. In cooperation with the National Institute of Justice and the National Institute of Drug Abuse, NIST has a four-part program for investigating analytical aspects of hair analysis. This program includes method development and evaluation, environmental issues research, interlaboratory studies, and reference material development.

Method development involves both investigations into extraction of drugs from hair and investigations of measurement methods. Acid extractions have been found to be effective for removing drugs from hair and are reproducible. Enzymatic digestions are more difficult to reproduce, but can be effective also. As is the case for urinalysis, GC/MS has proven to be a reliable method for detecting and quantifying the drugs in extracts from hair. The extracts can also be analyzed by immunoassay techniques or other mass spectrometric techniques, such as MS/MS. Attempts to analyze hair segments directly by direct probe MS/MS produced ambiguous results.

Research on environmental issues has focussed on investigations into distinguishing hair with external contamination of drugs from hair of drug users and investigations of the effects of various hair treatments on drug levels in hair. No washing procedures have been found that completely remove external contamination. The most effective procedures also extract drugs from within the hair. Detection of certain metabolites formed internally may prove to be the most reliable approach for proving drug use. One such metabolite is cocaethylene, believed to be formed in the liver when both cocaine and alcohol are present. We have found this metabolite in hair samples. Hair treatments such as shampoo, conditioner, and hydrogen peroxide have been found to significantly reduce cocaine levels in hair, but none of those investigated completely removed the cocaine, even after 30 treatments.

For the interlaboratory comparison studies, we sent unknown hair specimens to several laboratories and asked them to provide qualitative and quantitative information concerning their analyses. In two such exercises, involving 7-11 laboratories, qualitatively data were in general agreement, but quantitative results were very scattered.

As part of our effort to provide QA support to laboratories conducting hair analysis, we have developed a human hair powder reference material with measured concentrations of cocaine, benzoylecgonine, morphine, and codeine. GC/MS analysis of this material found the analytes to be homogeneously distributed in the material, thus allowing laboratories to evaluate the accuracy and reproducibility of their methods.

15. Certification of Five Clinically Significant Analytes in SRM 909a, Lyophilized Human Serum

A. Cohen, P. Ellerbe (Research Associate), L.T. Sniegoski, S. Tai (Research Associate), M.J. Welch, and E. White V

Standard Reference Material (SRM) 909a is a lyophilized human serum with certified concentrations of organic and inorganic analytes frequently measured in clinical laboratories. This SRM replaces SRM 909, which had been widely used by the clinical laboratory community for assuring the accuracy of reference and routine methods and secondary reference materials but is now out of stock. This new SRM consists of two lyophilized materials, one of which has most analyte concentrations in the normal range when reconstituted, while the other has elevated concentrations of most of the analytes.

Five organic analytes, cholesterol, glucose, creatinine, urea, and uric acid, have been certified in SRM 909a by scientists in the Organic Analytical Research Division. The methods used for certification all involve isotope dilution mass spectrometry and are recognized by the clinical laboratory community as "Definitive Methods". These definitive methods are highly accurate and precise methods that require specialized instrumentation and are not intended for routine use. The development of definitive methods at NIST has been the result of a cooperative effort between NIST and the College of American Pathologists, who sponsor two research associates at NIST. With these methods, it is possible to achieve relative standard deviations of 0.2-0.4% for independently prepared samples from a homogeneous serum pool.

For SRM 909a, 95% tolerance intervals around the mean values ranged from 1.2 to 1.7% for four of the analytes. The largest component of this imprecision is from vial to vial variations in fill weight. The other analyte, glucose, is subject to degradation with time, about 0.7% per year, in lyophilized serum. The 95% tolerance intervals were expanded for glucose to allow for degradation over a two year period. Nevertheless, these uncertainties are better than those routinely observed in the clinical laboratory. With two certified levels for most analytes, SRM 909a should be of considerable value to the clinical laboratory community and provide an accuracy base for the certified analytes in routine field measurements.

Work is underway to develop additional definitive methods for serum analytes. A method for triglycerides is ready for testing on serum samples. Work will begin next year on modifying the definitive method for total serum cholesterol for the determination of cholesterol associated with the lipoprotein fractions, HDL and LDL. With these methods it should be possible to accurately assign certified values to the key lipid indicators of heart disease risk.

16. Measurements of Carbonyl Sulfide in Automotive Emissions Using Tunable Diode Laser Absorption Spectroscopy

R.L. Sams

Carbonyl sulfide (COS) is the most abundant gaseous sulfur species in the earth's unpolluted atmosphere. This gas is believed to be the primary precursor of the stratospheric aerosol sulfate layer during non-volcanic time periods. Modelling studies have raised the concern that long term perturbations to this layer from increasing COS emissions could significantly influence the Earth's radiative budget and climate through increased solar scattering. The possibility of increased heterogeneous reactions on such aerosols can also lead to the potential for enhanced destruction of stratospheric ozone.

Measurements of COS were made over a period of several years at NIST and in collaboration with the National Center for Atmospheric Research (NCAR) in Boulder, CO. Both groups used tunable diode laser absorption spectroscopy (TDLAS) because of its high selectivity and sensitivity for detecting COS. Measurements were made on ambient COS as well as the emissions of numerous automobiles, both gasoline and diesel powered. The measurements at

NIST were made using the P(24) or P(25) transition in the 100-000 band of COS. The primary technique used was to split a portion of the infrared beam off to a line locking cell (containing COS) and use a first derivative frequency lock. The majority of the beam was passed through a long path cell (up to 200 m) and detected in the second derivative mode. The measurement were calibrated using low COS emitting permeation devices which were periodically weighed over several months to produce a steady emission rate of about 15 ng/min. The COS in clean ambient air was measured to be 500 ± 10 pptr. Measurements of automobile emissions of COS made both at NIST and NCAR, ranged between 2 and 300 ppb. Based on NCAR data concerning the average emission of the vehicles studied, about 50 ppb, and the total number of automobiles and trucks, about 200 million worldwide, the increase to the atmospheric budget per year from automobile and truck emissions will not exceed 0.1% of the nominal concentration of 500 pptr.

17. Preparation, Evaluation and Application of Nitric Oxide in Nitrogen Primary Standards

W.D. Dorko and W.J. Thorn III (Guest Scientist)

Nitric oxide (NO) is formed during the burning process within vehicular internal combustion engines and is therefore present in their exhaust emissions. It is considered to be a pollutant, and as such, is regulated under the terms of the Clean Air Act. Recent amendments to this Act have stipulated that the NO levels in vehicular exhaust be reduced and that the actual levels be determined with more accuracy. The USEPA, which must enforce the regulations, and the auto industry, which is required to meet the regulations, use NIST reference materials for NO in N_2 to calibrate their measurement instrumentation. The primary source of uncertainty in the certification of the SRM is associated with the primary standards used.

The primary standards used are gas mixtures of NO in N_2 prepared at NIST from pure NO and pure N_2 starting materials. Gas chromatography, mass spectrometry, Tunable Diode Laser Absorption Spectrometry (TDLAS) and chemiluminescence techniques were used for assaying the pure materials. A suite of standards ranging from 10% NO to 40 ppm NO was prepared by sequential gravimetric dilution in which the gases are weighed into high pressure gas cylinders. The overall error due to the weighing process did not exceed 0.15% relative down to the 40 ppm level. The intercorrelation of this suite of standards was accomplished by evaluating the response of an analytical instrument to the concentration determined from gravimetric data. Smaller sub suites of standards were used so that the signals generated by the lowest concentration in any suite were significant enough to measure with a precision of 0.2% relative. To attain this level of precision, the experimental design had to be altered, and the number of replicates increased so that the analytical time for each sub suite was increased from two to six hours. Portions of the sub suites were overlapped to produce an intercorrelation over the entire concentration range. This suite was used for the evaluation of SRMs ranging from 50 to 3000 ppm.

A more immediate concern of groups measuring auto exhaust is the concentration range from 1 to 10 ppm. To determine current measurement capabilities at these levels, an international round robin was organized by the Motor Vehicle Manufacturers Association (MVMA) for which NIST performed benchmark analyses of the circulated cylinder mixtures. It is not currently possible to produce cylinders containing primary standards of NO at these levels with the degree of certainty required. The reaction of NO with both the container walls and any traces of oxygen in the dilution gas preclude this. High precision and highly accurate dynamic dilution, using the new standards at the 50 ppm level as inputs, was therefore employed to establish the concentration of a set of working calibration standards for use in this work.

18. Long-Term Stability of Compressed Gas Mixtures Containing Low Concentration Volative Organic Compounds (VOCs)

G.C. Rhoderick and W.R. Miller

With the increase in the number and scope of federal and state programs implemented to monitor atmospheric pollutants, the need to measure low (ppb and pptr) levels of these Volatile Organic Compounds (VOCs) has become increasingly important. Certain VOCs are believed to pose a public health risk. Some have even been identified as possible cancer causing agents, while others (halogenated organic compounds) have been implicated as contributing to ozone depletion in the upper atmosphere.

To decrease human exposure to these compounds, regulations have been promulgated to reduce the amount of these substances released into the atmosphere. To order to meet these regulations, and to assess the long term trends in these atmospheric constituents, it is necessary to have both accurate and stable calibration gas mixtures.

Since the early 1980's, the National Institute of Standards and Technology (NIST) has been preparing, analyzing and certifying compressed gas mixtures that contain VOCs. Compressed gas mixtures containing up to twenty-six VOCs, in a balance of either air or nitrogen, have been prepared and/or analyzed at NIST. The mixtures are contained in aluminum cylinders which have had the interior walls passivated using a commercial, proprietary treatment process. The compounds included in these mixtures are various normal and branched alkanes, alkenes, aromatic and halogenated hydrocarbons. All of the compounds are in the concentration range of 0.1 - 3000 parts per billion (by mole) and the total uncertainty in the concentration of each is between ± 2 - 5%. The mixtures containing halogenated compounds were analyzed using a gas chromatograph equipped with an electron capture detector (GC/ECD), while those containing the other hydrocarbons were analyzed using a gas chromatograph equipped with a flame ionization detector (GC/FID). Calibration curves were generated using NIST primary standards.

To date, NIST has evaluated the stability of eight different groups of multi-component mixtures containing various combinations of 56 VOCs in passivated aluminum cylinders. Most of these compounds have exhibited excellent stability; some for periods of up to 6 1/2 years. Only one compound, propylene oxide, has consistently exhibited instability at both the ppm and ppb concentration levels. Another compound, 1,3-butadiene was stable at 1 ppm concentration levels but not at the 1 ppb level. Still, other compounds (i.e., ethylene oxide, carbon tetrachloride and bromomethane) are stable at the ppb concentration level in some, but not all, of the cylinders tested which seems to indicate that the stability of certain compounds is compromised by cylinder wall interactions.

19. Long-Term Stability and Performance of Sulfur Dioxide Permeation Tubes

G.D. Mitchell and P.A. Johnson

Sulfur dioxide (SO_2) permeation tubes, which are lengths of teflon tubing in which liquid SO_2 is sealed, have been extensively used for many years in dynamic dilution systems, as calibrants for detectors and measurement systems. Sulfur dioxide permeation tubes are available as SRMs from NIST and are certified by gravimetric measurements of weight loss over time. A study was undertaken to determine if, 1) the permeation rate is constant over the useful life of a tube and, 2) permeation characteristics of new batches of tubes have changed over the years.

The certificates for these SRMs (1625, 1626, and 1627) state that the useful life of the SRM is about 9 months, and that prior experiments have shown that the calibration remains valid as long as visible amounts of liquid sulfur dioxide remain in the tube. These prior experiments were completed over fifteen years ago and needed to be reexamined for the materials that are now being certified.

The first study was focused on the quantification of the permeation rate of new permeation tubes that are maintained at a single temperature until they are empty. Three sets of tubes were studied. Each set was identical and consisted of several tubes of 1, 2, and 5 cm lengths maintained at 20 °C, 25 °C, and 30 °C respectively. The data generated in this study was more precise than the data from the older study. Because of the improved precision, we were able to measure a small and gradual permeation rate decrease over the life of the tubes. The uncertainty in the rate due to this gradual decrease, which ranged from 0.5% to 2.0% relative, is being incorporated into the overall uncertainty given provided for the certified permeation rate of each tube.

The second study required the review of historical data, as well as the generation of new data, in order to determine if the material used to make the tubes has changed with time. The permeation rate of each tube was determined at 25 °C. A sub set of tubes was chosen and measured at 20 °C and 30 °C also, after which the data was used to determine the permeation range for the remainder of the tubes. The function used for this was determined a number of years ago, and this work was done to determine if it was still valid. The permeability coefficient was calculated for each SRM lot of tubes going back to 1982. This coefficient was calculated from the permeation rate of a tube at three different temperatures, 20, 25 and 30 °C, and the physical dimensions of the tube. The constancy of this coefficient shows that the tube material has remained the same. This is important criterion for providing long term continuity in the NIST SO_2 permeation tube certification program.

20. Bioassay Reference Values Established for Three NIST SRMs

W.E. May and S.A. Wise

Short-term bioassays are being used in many countries to evaluate the exposure of humans to complex mixtures of mutagens and potential carcinogens in air, water, soil and various emission sources. In 1987, the International Programme on Chemical Safety, in collaboration with the U. S. EPA and NIST, initiated an international collaborative study to determine the variability of data being generated by labs using the Ames Bioassay, the most frequently used mutagenesis bioassay. The study involved twenty laboratories from North America, Europe, and Japan that used the Ames test on a regular basis. Three NIST SRMs that are certified for chemical composition were used in the study: 1597, "Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar"; 1649, "Urban Particulate Matter"; and 1650, "Diesel Exhaust Particulate Matter".

The results from this study, presented at a recent meeting in Rome, revealed an interlaboratory variability (approaching 100% coefficient of variation) among the twenty study participants. While there exists a "true value" for chemical and physical properties that can be measured with a relatively high degree of accuracy and precision, bioassays are inherently more variable due in part to the fact that the living organisms that serve as detection devices are constantly undergoing dynamic processes of growth, replication, metabolism, and interaction.

The data from the collaborative study have been used to establish two types of reference values. One, expressed as a 95% confidence interval, defines the actual mutagenic activity as measured by the Ames bioassay test. The other, expressed as an 80% tolerance interval, characterizes the differences in reported mutagenic activity and establishes a realistic target for comparing results from the Ames bioassay with state-of-the-practice. With these Ames Mutagenicity reference values, SRMs 1597, 1649 and 1650 can now be used by the international bioassay measurement community as powerful tools for reducing the variability of Ames bioassay data.

C. Outputs and Interactions (Organic Analytical Research Division)

1. Publications

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Margolis, S.A., Jassie, L., and Kingston, H.M., "The Hydrolysis of Proteins by Microwave Energy," J. Automation Chem. 13, 93-95 (1991).

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Olsson, M., Sander, L.C., and Wise, S.A., "Comparison of the Liquid Chromatographic Behaviour of Selected Steroid Isomers Using Different Reversed-Phase Materials and Mobile Phase Compositions," J. Chromatogr. 537, 73-83 (1991).

Plant, A.L., Gray, M., Locascio-Brown, L., and Yap. W.T., "Hydrodynamics of Liposomes and Their Multivalent Interactions with Surface Receptors," Liposome Technology, 2nd Ed., CRC Press, Boca Raton (1991).

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Rebbert, R.E., Chesler, S.N., Guenther, F.R., Koster, B.J., Parris, R.M., Schantz, M.M., and Wise, S.A., "Preparation and Analysis of a River Sediment Reference Material for the Determination of Trace Organic Constituents," Fresenius J. Anal. Chem. (in press).

Rhoderick, G.C., "Development of a Gas Standard Reference Material Containing Eighteen Volatile Organic Compounds," Fresenius J. Anal. Chem. (in press).

Sander, L.C., Parris, R.M., Wise, S.A., and Garrigues, P., "Shape Discrimination in Liquid Chromatography Using Charge Transfer Phases," Anal. Chem. (in press).

Welch, M.J., Allgood, C.C., and Sniegoski, L.T., "Development of Methods and Standards for the Analysis of Human Hair for Drugs of Abuse, NIDA Monograph on Hair Analysis for Drugs of Abuse" (in press).

Wise, S.A., Benner, Jr., B.A., Christensen, R.G., Koster, B.J., Kurz, J., Schantz, M.M., and Zeisler, R., "Preparation and Analysis of a Frozen Mussel Tissue Reference Material for the Determination of Trace Organic Constituents," Environ. Sci. Technol. 25, 1695-1704 (1991).

Yap, W.L., Locascio-Brown, L, Plant, A.P., Choquette, S.J., Horvath, V., and Durst, R.A., "Liposome Flow Injection Immunoassay: Model Calculations of Competitive Immunoreactions Involving Univalent and Multivalent Ligands," Anal. Chem. (in press).

Zeisler, R., Koster, B.J., and Wise, S.A., "Specimen Banking at the National Institute of Standards and Technology," in Analytical Approaches as Related to Specimen Banking, M. Rossbach, P. Ostapczuk, and J.D. Schladot, Eds., Springer Verlag, Stuttgart, Germany (in press).

2. Talks

Benner, B., "Off-Line Supercritical Fluid Extraction of Standard Reference Materials," Third International Symposium on Supercritical Fluid Chromatography and Extraction, Park City, UT, January 14, 1991.

Brown, L., "Determination of Theophylline in Serum by Liposome-Based Flow Injection Immunoassay," Technical University of Munich, Munich, Germany, June 21, 1991. Invited

Brown, L., "Determination of Theophylline in Serum by Liposome-Based Flow Injection Immunoassay," Technical University of Budapest, Budapest, Hungary, June 24, 1991.

Brown Thomas, J.M., "Laboratory Automation of Fat-Soluble Vitamin Analyses," National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Washington, DC, April 2, 1991.

Christensen, R., "Current Practices in LC/MS," University of Ulm, Ulm, Germany, October 29, 1990. Invited

Christensen, R., "Homologous Internal Standards for Quantitative Analysis of Sugars in a Food Matrix by LC/MS," International Association of Environmental Analytical Chemists 7th LC/MS Symposium, November 1, 1990.

Choquette, S., "Optical Waveguide Chemical Sensor," NIST, Boulder, CO, July 7, 1991. Invited

Choquette, S., "Radiation Dosimetry Using Planar Waveguide Sensors," Society for Photo-Instrumentation Engineers, Boston, MA, September 4, 1991.

Craft, N., "Update on Carotenoid Reference Materials Program at NIST," National Feed Ingredient Association Meeting, Fort Lauderdale, FL, October 7, 1990. Invited

Craft, N., "Recent Developments in Carotenoid Analysis," Food & Drug Administration, Washington, DC, November 28, 1990. Invited

Craft, N., "Identification and Quantitative Determination of Beta-Carotene Isomers in SRM 968 and Normal Human Serum Using Multidimensional Chromatography," Federation of the American Societies for Experimental Biology, Atlanta, GA, April 23, 1991.

Dorko, W., "Gas Analysis Automation," CGA-Specialty Gases and Safety Seminar, Lanhorne, PA, October 10, 1990. Invited

Dorko, W., "NIST Atmosperic CO_2 Standards Program Accuracies and Uncertainties," WMO Meeting of Experts on CO_2 Measurement, Lake Arrowhead, CA, October 17, 1990. Invited

Dorko, W., "Stability of Cylinder Contained Gas Mixtures: Data from the NIST SRM and Re-Certification Programs," Generic Gas Cylinder Workshop, Boulder, CO, October 23, 1990. Invited

Dorko, W., "Generation of pptr Sulfur Gas Standards and Comparison with Eight Different Measurement Systems," Workshop on Verification of Analytical Methodology for Tropospheric Sulfur-Containing Gases: Recent Advances, Continuing Enigmas, and Future Directions, Menlo Park, CA, December 10, 1990. Invited

Dorko, W., "Work at NIST on Inorganic Gas Standards for Atmospheric Analysis," Annual Meeting of the NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO, March 4, 1991.

Dorko, W., "Work at NIST on Inorganic Gas Standards for Atmospheric Analysis," NIST, Boulder, CO, March 6, 1991. Invited

Dorko, W., "Preparation of Single Component Hydrocarbon Standards," International Hydrocarbon Intercomparison Planning Committee Meeting, NCAR, Boulder, CO, April 30, 1991. Invited

Dorko, W., "Preparation of Multicomponent Hydrocarbon Standards," National Center for Atmospheric Research, Boulder, CO, April 30, 1991. Invited

Dorko, W., "Multicomponent Non-Methane Organic Compound Mixtures for Use in Auto Exhaust Measurements," Calibration Gas Panel Meeting of the Motor Vehicle Manufacturers Association, Detroit, MI, May 3, 1991.

Emery, A., "Recovery of Diesel Fuel from Clay by Supercritical Fluid Extraction/Gas Chromatography," Association for Official Analytical Chemists, Phoenix, AZ, August 12, 1991.

Gray, M., "Flow Injection Immunoassay Studies of Cholesterol Related Lipoproteins" National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Washington, DC, April 2, 1991.

Guenther, F., "Chemistry for Profit, The State of the Environmental Lab Biz," NIST Division 835 Seminar, Gaithersburg, MD, March 25, 1991. Invited

Koster, B., "Sample Collection Procedures for the National Marine Mammal Tissue Bank," First International Symposium on Biological Environmental Specimen Banking, Vienna, Austria, September 23, 1991. Invited

MacCrehan, W., "Separation and Identification of the Organic Constituents of Gunshot and Explosive Residues by Micellar Electrokinetic Capillary Electrophoresis," High Performance Capillary Electrophoresis '91 Meeting, San Diego, CA, February 5, 1991

Margolis, S., "Assessment of HPLC Method of Analysis of FMOC Derivatives of Amino Acids and the Measurement of Trace Impurities in Amino Acid Samples," Federation of the American Societies for Experimental Biology, April 24, 1991.

May, W., "Standard Reference Materials for Chemical and Biological Studies of Complex Environmental Samples," International Programme on Chemical Safety Meeting, Rome, Italy, November 5, 1990. Invited

Miller, W., "Analysis and Stability of Compressed Gas Mixtures Containing Non-Methane and Volatile Organic Compounds," Measurements of Toxic and Related Air Pollutants Meeting, Durham, NC, May 10, 1991

Mitchell, G., "Determination of Atmospheric Level of CO_2 in Compressed Gas Cylinder by Coulometric Titration,"National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Washington, DC, April 2, 1991.

Rhoderick, G., "NIST Standards of Non-Methane Hydrocarbons for Ambient Air Measurement," NIST, Boulder, CO, March 6, 1991.

Sander, L., "Shape Selectivity in Liquid Chromatography," Chromatography Forum of the Delaware Valley, Malvern, PA, February 21, 1991. Invited

Sander, L., "Shape Selectivity in Liquid Chromatography," Rohm & Haas Company, Springhouse, PA, February 21, 1991. Invited

Sander, L., "Molecular Shape Discrimination in Liquid Chromatography for the Separation of Aromatic Compounds," American Chemical Society National Meeting and 4th Chemical Congress of North America, New York, NY, August 28, 1991. Invited

Sniegoski, L., "Isotope Dilution-Mass Spectrometric Determination of Drugs of Abuse in Hair," 14th International Symposium on the Synthesis and Application of Isotopes and Isotopically Labelled Compounds," Toronto, Canada, September 3, 1991.

Welch, M., "The Analysis of Human Hair for Drugs of Abuse by GC/MS," Howard University, Washington, DC, February 15, 1991. Invited

Welch, M., "Analysis of Human Hair for Drugs of Abuse," American Society for Mass Spectrometry and Allied Topics Conference," Nashville, TN, May 21, 1991

Wise, S., "Investigations of Selectivity in Reversed-Phase Liquid Chromatography," Rutgers University, NJ, October 18, 1990. Invited

Wise, S., "Standard Reference Materials for Organic Environmental Measurements," 1990 Environmental Analytical Chemistry Symposium, Tamkang University, Tamsui, Taiwan, December 15, 1990. Invited

Wise, S., "Specimen Banking--A Complement to Traditional Environmental Monitoring, Brigham Young University, Provo, Utah, March 18, 1991. Invited

Wise S., "HPLC Analysis of Polycyclic Aromatic Hydrocarbons," LabTech 91, Atlantic City, NJ, June 14, 1991. Invited

Wise, S., "PAH Analysis Using HPLC: An Overview," Environmental Symposium, Perkin Elmer, Rockville, MD, September 17, 1991. Invited

Wise, S., "Determination of PCBs and Chlorinated Pesticides in Marine Mammal Tissues," First International Symposium on Biological and Environmental Specimen Banking, Vienna, Austria, September 23, 1991. Invited

Wise, S., "Specimen Banking--A Complement to Traditional Environmental Monitoring, "First International Symposium on Biological and Environmental Specimen Banking," Vienna, Austria, September 25, 1991.

Wise, S., "Current Activities within the National Biomonitoring Specimen Bank, "First International Symposium on Biological and Environmental Specimen Banking," Vienna, Austria, September 24, 1991.

Wise, S., "Determination of Inorganic Constituents in Marine Mammal Tissues, "First International Symposium on Biological and Environmental Specimen Banking," Vienna, Austria, September 25, 1991.

3. Committee Assignments

J. Brown Thomas

Fund Raising, NIST Child Care Center (Chairman)

N.E. Craft

Steering Committee, Carotene Research Interactive Group
Associate Editor, Carotenoid News
Carotenoid Analytical Methods Committee, National Feed Ingredient Association

W.E. May

ACS Analytical Chemical Division Education Committee
Special Topics Sub-Committee Chairman, International Polycyclic Aromatic Hydrocarbons Society
Board of Governors, International PAH Symposium
Program Committee Chairman, International PAH Symposium
Editorial Board, Journal of PAC
Interdepartmental Minority Health/Science Careers Coordinating Committee
NIST SES General Performance Review Board
Toxic Substances Control Act, Interagency Testing Committee (DoC Representative)

R.M. Parris

Washington Chromatography Discussion Group (Secretary)
NIST CSTL Quality Assurance Committee
NIST SEBA Executive Board

L.C. Sander

Washington Chromatography Discussion Group (President)
NIST Research Advisory Committee

L.T. Sniegoski

Bookkeeper, NIST Child Care Center

M.J. Welch

Standards Committee of the American Association for Clinical Chemistry
Advisor to Standards Committee of the College of American Pathologists
NCCLS Subcommittee on Urine Drug Testing

S.A. Wise

Sub-Committee on Chromatography, International Committee on Polycyclic Aromatic Hydrocarbons (Chairman)

Publicity Committee, Division of Analytical Chemistry, American Chemical Society (Chairman)

Editorial Advisory Board, Fresenius' Journal of Analytical Chemistry

4. Others

a. Seminars

October 3, 1990

Bulvindar Kaur, Shandon Scientific, Ltd., Cheshire, England, Talk entitled: "Development and Applications of Porous Graphitic Carbon in Liquid Chromatography" (Division Sponsor: L.C. Sander)

October 29, 1990

Paul Becker, NOAA, Anchorage, AK, Talk entitled: "Alaska Marine Mammal Tissue Archival Project" (Division Sponsor: S.A. Wise)

October 30, 1990

Joe Hedrick, Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, VA, Talk entitled: "Adventures in SFE" (Division Sponsor: W.A. MacCrehan)

November 16, 1990

Apryll Stalcup, University of Hawaii, Honolulu, HI, Talk entitled: "Cyclodextrins in Liquid Chromatography" (Division Sponsor: S.A. Wise)

March 1, 1991

Laura McConnell, Department of Chemistry, University of South Carolina, Talk entitled: "Air-Water Exchange of Hexachlorocyclohexane in the Great Lakes," (Division Sponsor: S.A. Wise)

March 5, 1991

Ray P.W. Scott, Georgetown University, Washington, DC, Talk entitled: "Column Design in Liquid Chromatography" (Division Sponsor: W.A. MacCrehan)

March 25, 1991

Franklin Guenther, Coast to Coast Analytical Services, San Luis Obispo, CA, Talk entitled: "Chemistry for Profit, The State of the Environmental Lab Biz" (Division Sponsor: S.A. Wise)

March 27, 1991

Stephen Scharf, Cetus Corporation, Emeryville, CA, Talk entitled: "The Polymerase Chain Reaction: How You Can Use PCR for Everything from Cloning your Genes to Figuring Out Whodunit" (Division Sponsor: W.A. MacCrehan)

April 24, 1991

Gary Byrd, R.J. Reynolds Co., Talk entitled: "Application of Thermospray LC/MS to Metabolism Studies" (Division Sponsor: M.J. Welch)

July 24, 1991

Lisa Goebel, Virginia Tech, Talk entitled: "Electrokinetic Capillary Separations Involving Ionic and Non-Ionic" (Division Sponsor: W.A. MacCrehan)

August 16, 1991

Nobuo Tonaka, University of Japan, Kyoto, Japan, Talk entitled: "TEM Study of Wide-Pore Packing Materials, and Charge-Transfer-Type Stationary Phases for the Separation of Chlorinated Dioxin Isomers" (Division Sponsor: S.A. Wise)

b. Conferences/Workshops Sponsored/Co-Sponsored

October 31, 1990

1st CAALS Workshop on Supercritical Fluid Extraction, NIST, Gaithersburg, MD

November 15, 1990

NIST/NCI Micronutrient Analysis Workshop, NIST, Gaithersburg, MD

December 10-12, 1990

NOAA Quality Assurance Workshop, Seattle, WA

April 19, 1991

The Analysis of Hair for Drugs of Abuse, NIST, Gaithersburg, MD

June 24, 1991

Moisture in Oils Workshop, NIST, Gaithersburg, MD

c. SRM Activities

39j Benzoic Acid Purity [certified]
909a Human Serum Certification of five organics [certified]
968a Fat-Soluble Vitamins in Serum [certified]
1494 Aliphatic Hydrocarbons in 2,24-Trimethylpentane [in progress]
1507b THC in Urine [certified]
1508 Cocaine and Be in Urine [certified]
1586 Isotopically Labeled and Unlabeled Priority Pollutants in Methanol [stability checked]
1588 Organics in Cod Liver Oil [stability checked]
1163 Sulfur Dioxide in Nitrogen, 1500 ppm [in progress]
1625 Sulfur Dioxide Permeation Tube, 10 cm [certified]
1626 Sulfur Dixoide Permeation Tube, 5 cm [certified]
1627 Sulfur Dioxide Permeation Tube, 2 cm [certified]
1629 Nitrogen Dioxide Permeation Tube, 2 cm [certified]
1665 Propane in Air, 3 ppm [in progress]
1666 Propane in Air, 10 ppm [in progress]
1667 Propane in Air, 50 ppm [in progress]
1679 Carbon Monoxide in Nitrogen, 100 ppm [in progress]
1681 Carbon Monoxide in Nitrogen, 1000 ppm [in progress]
1685 Nitric Oxide in Nitrogen, 250 ppm [in progress]
1686 Nitric Oxide in Nitrogen, 500 ppm [in progress]
1687 Nitric Oxide in Nitrogen, 1000 ppm [in progress]
1693 Sulfur Dioxide in Nitrogen, 50 ppm [in progress]
1694 Sulfur Dioxide in Nitrogen, 100 ppm [in progress]
1696 Sulfur Dioxide in Nitrogen, 3500 ppm [in progress]
1939 Polychlorinated Biphenyl (Congeners) in River Sediment A [certified]
1941a Organics in Marine Sediment [in progress]
1974 Organics in Mussel Tissue [certified]
2260 Aromatic Hydrocarbons in Toluene [certified]
2261 Chlorinated Pesticides in Hexane [certified]
2381 Opiates in Urine [certified]
2382 Morphine Gluturonide in Urine [certified]
2389 Amino Acid Standard Mixture [in progress]
2619 Carbon Dioxide in Nitrogen, 0.5% [in progress]
2620 Carbon Dioxide in Nitrogen, 1.0% [in progress]
2623 Carbon Dioxide in Nitrogen, 2.5% [in progress]
2627 Nitric Oxide in Nitrogen, 5 ppm [certified]
2628 Nitric Oxide in Nitrogen, 10 ppm [certified]
2629 Nitric Oxide in Nitrogen, 20 ppm [certified]
2631 Nitric Oxide in Nitrogen, 3000 ppm [in progress]
2636 Carbon Monoxide in Nitrogen, 250 ppm [in progress]
2637 Carbon Monoxide in Nitrogen, 2500 ppm [in progress]

2638 Carbon Monoxide in Nitrogen, 5000 ppm [in progress]
2639 Carbon Monoxide in Nitrogen, 1% [in progress]
2730 Hydrogen Sulfide in Nitrogen, 5 ppm [certified]
2731 Hydrogen Sulfide in Nitrogen, 20 ppm [certified]
2727 Carbon Monoxide & Propane & Carbon Dioxide in Nitrogen, 1.6, 0.6 & 11% [certified]
2728 Carbon Monoxide & Propane & Carbon Dioxide in Nitrogen, 8, 0.3 & 14% [certified]

PROCESS MEASUREMENTS

VI. Process Measurements Division (836)

Hratch G. Semerjian, Chief

A. Division Overview

The Process Measurements Division develops new and improved measurement techniques, standard measurement practices and relevant mathematical models to describe and interpret the performance of laboratory and process instruments for measurement, analysis and control of industrial processes. Emphasis is placed on measurement methods and data that are needed for process control in the chemical, biochemical, and related industries, with a special emphasis on the development of on-line, and where possible *in-situ*, measurement techniques. Measurements of interest include fluid flow rate, liquid density and volume, humidity, chemical composition, pH, particle size, number density and volume fraction, velocity, temperature, dynamic pressure and other quantities of interest in multiphase reacting and non-reacting process streams.

Accurate measurements for **process and quality control** require validation of measurement methods and calibration of instruments using techniques traceable to national standards. Therefore, calibration services and related research efforts represent a very important part of our activities. The Division provides measurement services for fluid flowrate, liquid density, volume, airspeed, humidity, and temperature measurements for a wide range of clients across the country. Efforts are continuing towards full implementation of the new International Temperature Scale (ITS-90) at NIST and dissemination of information on the scale and guidelines for implementation. Several articles and notes have been published in professional and trade journals, and numerous talks and lectures have been presented across the country at conferences, seminars and workshops. A comprehensive report (NIST Technical Note 1265) has been published to provide guidelines for realizing the ITS-90 scale in industrial and other standards laboratories. Currently, we have realized the ITS-90 in our laboratory for the temperature range from 84 to 1235 K. Two new facilities are being developed to realize ITS-90 below 84 K.

In spite of the fact that the thermocouple has been replaced by the Standard Platinum Resistance Thermometer (SPRT) as the defining instrument for ITS-90, it is still used widely in industry. Therefore, we have undertaken a major effort to determine the emf values as a function of T_{90} for all the ISA letter-designated thermocouple types. To derive new accurate reference functions for them, an international effort is under way for interlaboratory comparisons, coordinated by NIST. Analyses of the experimental data and derivation of the reference functions are in progress; the results of this monumental task will be published as NIST Monograph 175.

Humidity measurement is another area where a major effort is under way to improve our capabilities to meet the new measurement needs of U.S. industry. Currently, humidity calibrations are performed using two-pressure humidity generators that cover the concentration range of 3 ppmv (-70 °C dewpoint temperature) to normal atmospheric levels. Extension of the measurement range to concentration levels of 20 ppbv is required to enable the semiconductor industry to accurately monitor water contamination in process gasses, which is considered to be one of the primary causes of manufacturing defects in semiconductors. At present, no standards exist to validate the performance of new instruments below the ppmv range. We have con-structed a low-frost point humidity generator that will operate over the range 20 ppbv (-100 °C dewpoint temperature) to 1000 ppmv. A new gravimetric hygrometer is being constructed to characterize the humidity generator. When completed, this facility will represent the only humidity measurement standard available for the sub-ppm range, and will be a very important tool for quality control in the semiconductor manufacturing industry.

In the area of flow metrology, we are continuing to investigate the effect of "non-ideal" installations on the performance of flowmeters in industrial settings. Laser velocimetry measurements have been performed to study the effects of the flow field upstream of a flow measurement device on its performance. This project has resulted in the development of experimental data and predictive capabilities critically needed for improvement of the current flowrate measurement technology, and establishment of new U.S. flow metering standards.

There are several other efforts aimed at improving and expanding our measurement services. We are upgrading and automating our laboratories used for calibration of high temperature thermocouples, liquid-in-glass thermometers, low-temperature thermocouples, industrial PRT's, thermistors, and gas flowmeters. We have succeeded in improving the performance of our new volumetric liquid flowrate calibration facility, and ensured internally consistent measurements with gravimetric facilities. We have completed a project to establish an improved liquid density measurement capability, with uncertainties at or below the ±0.01% level. This will also have a direct impact on the accuracy of gravimetric and volumetric calibration facilities for liquids. We are also interacting with the American Petroleum Institute (API) to begin an effort to decrease, by a factor of two, the current uncertainty level for calibration of liquid volumetric test measures. Such advances would significantly benefit API member companies involved in the custody transfer of petroleum products in the U.S. and in the international marketplace.

In addition to development of measurement standards and calibration services, a very significant part of our research involves the development of **new measurement techniques** and data for improved process measurements. Our research on optical measurement techniques for applications in single and multiphase reacting flows is recognized worldwide. Characteristics of liquid sprays and spray flames are investigated using phase/Doppler and laser velocimetry techniques, which provide detailed data on droplet size, number density, and velocity. Lack of reliable measurements and national standards for these important process parameters has hampered the development of a fundamental understanding of two-phase reacting flows. Several efforts are being coordinated through ASTM and DoE Working Groups to address these shortcomings. Light scattering techniques are also being utilized to study the structure of spray flames fueled by model alternative fuels, and to assess the potential for improvements in energy efficiency and pollutant emissions.

Coherent Anti-Stokes Raman Spectroscopy (CARS) is finding wide usage for temperature and composition measurements in complex reacting flows. The recently developed NIST high resolution CARS spectrometer system has been applied in a successful experimental validation of the first *ab initio* calculation of the pressure induced collapse of the spectrum of CO. This work, in collaboration with NASA Goddard, demonstrates the accuracy of the physical model which underlies the use of the CARS spectra of molecules like N_2 and CO for temperature and pressure measurements.

CARS will also be utilized to develop a primary standard for dynamic calibration of transient temperature and pressure transducers; such a capability does not currently exist in the U.S. A Workshop on the Measurement of Transient Temperature and Pressure, held at NIST in April 1991, examined the problems associated with the absence of any national standards for transient pressure and temperature measurements, and established the need for dynamic measurement standards. At least 15 laboratories have already volunteered to participate in round-robin intercomparisons of transducer "calibrations". A second workshop will be held as part of the Temperature Symposium in April 1992, to establish a broader base of support for this effort.

Over the last two years, we have made a significant effort to reevaluate the overall direction of the Division's research, and to focus our work on those areas where it would have the most significant impact and meet new or future needs of U.S. industry. As a result of these deliberations, we have identified **thin film sensors, materials synthesis, semiconductor fabrication**, and **industrial waste minimization** as areas of future thrust. These areas were selected because of their importance for competitiveness of the U.S. industry as well as the existing expertise within our Division, both experimental and computational, which could be utilized for rapid progress and productive research. Major budget initiatives in these areas have already been put forth, jointly with other NIST Laboratories, or are being planned for the near future.

Thin films are expected to find increasing applications in process sensing, as requirements for selectivity and time response become more demanding. Several projects are underway to exploit the unique characteristics of thin films. Thin film thermocouples have been developed for a variety of applications and new materials have been investigated for thermocouples with higher voltage output. As part of the DoE/NASA/Cummins adiabatic engine program, sputter deposited thin film thermocouples, placed on the surface of test plugs inserted into a diesel engine combustion chamber, have been developed for direct monitoring of surface temperatures.

A new ultrathin film chemical sensors laboratory was completed that combined existing surface analytical facilities with new deposition and characterization capability. SnO_2 films of several hundred angstrom thickness have been sputter deposited on c-axis sapphire and shown to have epitaxial structure. In addition, in a collaborative effort with Northwestern University, thicker films were produced using organometallic chemical vapor deposition (OMCVD) methods. Fabrication of crystalline films is a basic requirement for future development of multi-sensor arrays compatible with microelectronic fabrication technologies. The feasibility of a new gas sensing structure based on diode characteristics has been shown using TiO_2 and metallic contacts. The rectifying behavior of this structure shows high sensitivity to gas exposure, ranging from strong rectification to ohmic characteristics. Investigation of similar response characteristics using SnO_2 is underway.

We have also investigated self-assembled organic monomolecular films for a variety of applications both for sensing and biotechnological application, e.g., adsorption of proteins on tailored surface functionalities. This year's research has focussed on the interaction of self-assembled monomolecular films with other materials. The first successful report of adsorption of a large protein on these structures was published by NIST this year; in this work a monolayer of cytochrome-c was attached to the surface of a thiol monolayer attached to a gold substrate. Through collaborative efforts with industrial firms, investigation of fluorinated species has also been started.

Several of our new and current projects are addressing problems associated with **high temperature materials synthesis**. During the past year, the first phase of a consortium project on the Supersonic Inert Gas Metal Atomization (SIGMA) process was completed. This is one of the most promising processes for production of high temperature ceramic and metal powders with unique microstructural properties. Recent experiments have demonstrated the feasibility of performing on-line measurements of size distribution of powder particles, which can be utilized for feedback control. In addition, detailed models have been developed to predict the supersonic flow field that leads to liquid metal jet break-up and atomization, which is a critical component of the expert system used for process control. Such on-line measurement and control capabilities are expected to lead to improved product quality and process efficiency.

A new high temperature aerosol process has been developed to produce fine (submicron) powders of the high T_c superconductor YBaCuO. The production of this material, which displayed a well-defined superconducting transition at 92 K, is an example of the control of purity and stoichiometry which can be realized under flame processing conditions, and is indicative of the potential that flame processes may hold for bulk processing of high temperature superconductors and other materials. In addition, we have completed the design and assembly of a unique high temperature flow reactor, which allows molecular beam sampling and provides optical access to study the dynamics of elementary reactions relevant to materials synthesis and semiconductor manufacturing.

We have had a significant increase in our interactions with the **semiconductor** industry, and the government/industry consortium SEMATECH. Based on these interactions, a broad range of research activities have been proposed both for internal and external funding. As mentioned before, development of new humidity measurement capabilities will support the need of the semiconductor industry for low moisture concentration measurement standards and instruments. A NIST/SEMATECH sponsored workshop on the state-of-the-art of mathematical modelling has emphasized the need for detailed chemical kinetics data and modeling for plasma processes, physical plasma modeling, and development of measurement techniques for application to plasma and CVD reactors. We have just completed a SEMATECH funded project to assess selected process control sensors for plasma processing of semiconductor materials, primarily etching reactions for silicon and related species.

There is also significant interest in improving temperature and gas flow rate measurements, in order to optimize deposition and etching processes. Recent interactions with semiconductor manufacturing companies have indicated that gas flow measurement problems are seriously affecting quality control and reject rate, hence the international competitiveness of the U.S. microelectronics industry. In response, we have initiated several proposals to assess and quantify gas measurement performance of flowmeters and laboratory facilities; we have just been informed that SEMATECH has agreed to fund this effort.

A new and highly promising approach to understanding cluster growth kinetics and their role in film growth has been realized by means of molecular dynamics simulations. Simulations of atom-cluster and cluster-cluster collisions have demonstrated high sticking probabilities and rapid accommodation of excess energy. This new approach to cluster kinetics holds promise for understanding film growth resulting from cluster-surface collisions. It also provides the basis for modelling the growth of particulates from the gas phase in CVD and plasma reactors, which is one of the main sources of wafer contamination. The information generated by this project has already been utilized for process optimization by semiconductor manufacturers.

We are also providing critically needed data and new measurement techniques to address a major national concern - disposal of **hazardous industrial wastes**. An existing high temperature fluidized bed (FB) reactor facility has been modified to study pyrolysis and combustion of chlorinated hydrocarbons. The major thrust of the project is the application of advanced on-line diagnostics (e.g., FTIR) for measurement of selected model compounds, reaction intermediates and final oxidation products in multicomponent systems. A new project has also been initiated on corrosion/erosion testing of structural materials (metals and ceramics) in FB environments containing chlorine species at elevated temperatures.

A related new thrust is the application of SuperCritical Water Oxidation (SCWO) reactions for disposal of hazardous industrial wastes. Enhanced solubility of organic compounds, increased reaction rates encountered at high fluid densities, and reduced mixing times due to the single phase nature of the mixture make this process an ideal solution for many industrial waste disposal problems. NIST is in an excellent position to address this interesting and nationally important area of research because of the critical nucleus that exists within CSTL with expertise in supercritical fluid properties, chemical kinetics of high density systems, and reacting flow systems. A supercritical water flow-reactor with optical access to allow optical measurements of phase, chemical species, and reaction products (and intermediates) has been designed and is currently under construction. This reactor will allow in situ CARS, spontaneous Raman, LIF, optical absorption and scattering studies under conditions appropriate to SCWO. In addition, a second flow reactor is being assembled for complementary studies of global kinetics, reactor-material durability, and process efficiency. The reactor has been designed for studies of oxidative destruction of dilute solutions of compounds at temperatures up to 700 °C and pressures up to 40 MPa, and the associated analytical instrumentation is being assembled.

Many of our experimental efforts are complemented with **computational models** to simulate chemically reacting flows, formation and oxidation of particles, and transport processes in high temperature reacting flows. Our numerical model for an axisymmetric jet diffusion flame has produced results which are in excellent agreement with experimental observations made at Wright Research and Development Center. Similar techniques are being applied towards modelling of CVD processes and combustion of chlorinated hydrocarbons. A flow model for a pedestal CVD reactor has been developed this year; preliminary results compare very favorably with experimental measurements provided by Sandia National Labs. A new thrust in this area will involve the study of the fate of particles in CVD reactors. Results of this study will bear directly on the wide-spread problem of particulate contamination of CVD films. An interactive graphics post-processor, developed to permit analysis of the outputs of large scale kinetics calculations, has been applied to identify a reliable reduced-set of reactions for the decomposition of silane, the principal reactant in silicon CVD. With this reduced set, it will be possible to construct fluid flow models with accurate chemical kinetics and thereby provide more realistic process models for CVD reactors.

As part of our expanded responsibilities and revised mission statement associated with the new National Institute of Standards and Technology, we are making an effort to increase our interactions with industry, and striving to develop and maintain all possible forms of **technology transfer**. Industrial consortia have been one of the most successful forms of this transfer and our "Flowmeter Installation Effects" consortium has attracted a significant number of new members. The NIST consortium project on "Intelligent Processing of Materials" has started its second phase with wider industry participation. We have established new collaborative efforts with several chemical and instrumentation companies, universities and national laboratories. We have also utilized workshops (on CVD processes, dynamic measurements, etc.) and short courses (on precision thermometry, flow measurements, humidity, etc.) to asses industry needs and transfer know-how to industrial users. We have also organized two international conferences, the International Conference on Liquid Atomization and Spray Systems (ICLASS-91), held at NIST in July 1991, and the Seventh International Symposium on Temperature: Its Measurement and Control in Science and Industry, to be held in April 1992. Standards writing and trade organizations, and professional societies (such as ASTM, ASME, ISA, AIChE, API, AGA, GRI) have also provided a forum for transfer of NIST technology to the U.S. industry.

During the past year, outstanding accomplishments of our technical staff have been recognized with many awards. Dr. Billy Mangum has been selected to receive the Department of Commerce Gold Medal Award for his seminal work on the ITS-90; Drs. George Mattingly and Cary Presser, and Mr. Pedro Espina have received a DoC Group Silver Medal Award, with their coworkers in MSEL and MEL, for their research on the SIGMA process; and Dr. Steve Semancik received the DoC Bronze Medal Award for his outstanding contributions in the area of chemical sensors. In addition, George Burns and Paul Baumgarten have received NIST Measurement Service Awards to recognize their efforts to provide high quality measurement services in thermometry and flow metrology, respectively.

During FY91, some organizational changes occurred within our Division, as a result of the formation of the Chemical Science and Technology Laboratory. The Bioprocess Metrology Group was transferred to the newly created Biotechnology Division. In addition, the Optical Measurements Group was combined with parts of the Reacting Flow Diagnostics Group. As a result, the Division is currently organized into five Groups: Fluid Flow, High Temperature Processes, Reacting Flows, Process Sensing and Thermometry. The following pages describe the activities of these Groups, and their major accomplishments and future plans.

B. Selected Technical Reports (Process Measurements Division)

1. Calibration and Test Services Performed by the Process Measurements Division

B.W. Mangum, G.E. Mattingly, and J.R. Whetstone

In the past year, The Process Measurements Division has provided calibration services in response to industry and government requests for a number of metrological tasks in the areas of temperature, humidity, fluid flow rate, air speed, and liquid density and volume measurements. In addition, our capabilities, experimental techniques and facilities used to perform these services are being upgraded, and improvements in measurement uncertainties have been reported in the literature. The specific calibration services offered to U.S. industry and other laboratories are summarized below:

Service	Number of Items Calibrated	
Fluid Flowrate	36	(29 for industry)
Volumetric Containers	83	(71 for industry)
Aerodynamic Devices	54	(48 for industry)
Reference Standard Hydrometers	73	(73 for industry)
Humidity	51	(39 for industry)
Standard Resistance Thermometers	140	(96 for industry)
Thermocouples	228	(221 for industry)
Laboratory Thermometers	463	(413 for industry)

These calibrations generally establish a traceability link between the national standards maintained by NIST and the standards of the requesting laboratories. In this way, a basis is provided for the assurance of all the measurements produced in the requester's laboratories.

Since the new International Temperature Scale of 1990 (ITS-90) came into effect in January 1990, the number of thermometry calibrations provided has continued to increase. The calibration of Standard Platinum Resistance Thermometers (SPRTs) and High-Temperature SPRTs (HTSPRTs) on the ITS-90, as defined over the range from 83.81 K to 1234.93 K, continued at a record level in FY91. There were also several comparison calibrations of capsule-type SPRTs, rhodium-iron resistance thermometers (RIRTs) and germanium resistance thermometers (GRTs) against the NIST-ITS-90 reference scale in the region 0.65 K to 83.81 K. A Measurement Assurance Program (MAP), covering the range from Ar (83.81 K) to Zn (419.53 °C), was completed with the U.S. Army TMDE Support Group, Redstone Arsenal. In addition, we designed and initiated a special MAP with the NASA Stennis Space Center in a round robin measurement of 3 SPRTs at the triple-point temperature of water (273.16 K), with NIST and various NASA calibration facilities participating.

Currently, humidity calibration services are offered in the dewpoint temperature range of -70 °C to +40 °C using our two-pressure humidity generator. A new gravimetric hygrometer has been designed and is now under construction. Its purpose is to provide the means to make the absolute measurements of moisture concentration required in commissioning the low-frost point humidity generator. This generator will extend NIST's ability to provide standards for moisture concentration measurements from the current level of 3 ppmv to approximately 20 ppbv (dewpoint temperature of -100°C). Initial operational testing of the low frost-point generator and comparison with the two-pressure generator are planned for FY92.

2. Flowmeter Installation Effects

T.T. Yeh, G.E. Mattingly, and B.L. Shomaker

The increasing scarcity of fluid resources and value of fluid products have led to an increased demand for improved flow measurements - especially in the chemical process industries. More accurate measurements are needed for improved material accountability for custody transfer of products, and better precision is needed for improved process control and optimization. These needs involve: (1) adding flowmeters to systems where previously they were not considered necessary or where measurements were not feasible; (2) increasing the accuracy of existing meters; or (3) replacing installed meters with more accurate devices. Where flow meters are being retrofitted into systems not designed for "ideal" flowmeter installation conditions, or where increased levels of accuracy are desired for existing meters, the currently available installation standards and specifications give little or no guidance to attain desired levels of performance. These needs are being addressed through our programs on flowmeter installation effects which will benefit new standards being written for U.S. flowmetering practices.

The pipe flow measurement program being conducted by the Fluid Flow Group is continuing in its sixth year with the support of an industry-government consortium which includes flowmeter manufacturers and users - both U.S. and foreign. This research program uses Laser Doppler Velocimetry (LDV) in a water flow facility to characterize pipeflows downstream of selected piping configurations known to disturb flowmeter performance. The configurations investigated to date have included the single elbow, several arrangements of the two elbows-out-of-plane configuration, and the tee used as an elbow. These pipeline elements have been studied with and without conventional flow conditioning devices. Results quantify pipeflow profiles for both time-averaged and turbulent velocity components as well as swirl-angle and velocity spectra. These results have produced, for the first time, a fundamental understanding of these secondary flows, which has led to improved flow measurements for several types of flowmeters.

Currently, we are assessing the pipe flows produced by a pipeline reducer. This device is often used upstream of a meter to enable a smaller, less expensive meter to be used in its high flow range where performance is best. Currently, this program includes an assessment of the effects of this reducer on orifice and turbine flow meters. The results of this program will provide: (1) improved fluid flowrate measurements impacting industrial productivity and international competitiveness; (2) direct input into the new American metering standards for flowmeter installation effects; and (3) data for validation of computational models to describe and understand pipeflow phenomena. These measurements are also being used to assess and quantify the feasibility of using non-ideal pipe flows to serve as fluid mixing environments. This program involves collaborative interactions with the flow research program under way at NIST-Boulder.

3. Supersonic Inert-Gas Metal Atomization (SIGMA)

P.I. Espina, S.M. Huzarewicz, G.E. Mattingly, C. Presser, S.D. Ridder (MSEL), F.S. Biancaniello (MSEL), and S. Osella (MEL)

The Process Measurements Division has participated in several aspects of a project on Supersonic Inert-Gas Metal Atomization (SIGMA), supported by an industry-government consortium. The goal of the current phase of this project is to control and optimize metal powder atomization processes using expert systems. The SIGMA process is industrially attractive because of its efficiency in producing metal powders with unique micro-structural properties. Such powders enable critical components such as turbine blades, valves, bearings, etc., to have improved strength and corrosion resistant properties. Because of the complexities of the SIGMA process, NIST teams from CSTL, MEL, and MSEL participate in this joint effort. During the past year, the CSTL contribution came from two Groups in the Process Measurements Division.

The Fluid Flow Group has adopted the research strategy of focussing first on the simpler flow processes, by studying the gas and liquid streams separately using both optical and intrusive measurement techniques and computational fluid dynamics (CFD). Shadowgraphy, Schlieren and holographic studies have been carried out in both the gas-only and gas-liquid flows. Results have shown that this powder production process is an extremely rapid and complex one, where the gas stream breaks up the liquid jet in a highly dynamic manner. The liquid droplet formation process occurs through a series of stages, and ultimately produces the small droplets which are rapidly solidified. Theoretical analyses were performed on critical features of the more complicated gas-only flows. These analyses included application of the method of characteristics to a simplified gas-only flow field. Results approximated experimental measurements well, and this technique was a very cost effective way for consortium members to assess other atomizing gas arrangements. CFD studies can also be used to produce modified atomizer arrangements which are more stable and controllable. Finally, high speed photographic techniques have been used for qualitative - and to some degree the quantitative - characterization of the critical flow fields in the actual SIGMA process and to enhance the feasibility to control and optimize the process.

The High Temperature Processes Group has completed the adaptation of a commercial instrument, based on laser diffraction, for on-line measurement of solidified metal particles. This involved a major modification of computerized data processing method, whereby a direct solution technique was used to reduce the data acquisition time by an order of magnitude and to allow the instrument to be used as a process control sensor.

4. Particulate and Droplet Diagnostics in Spray Flames

C. Presser, J.R. Zurlo, A.K. Gupta, H.G. Semerjian, and C.T. Avedisian (Cornell Univ.)

The overall objective of this project is the development and application of advanced, laser-based measurement techniques for study of spray flames. The direct result of this continuing effort has been an increased fundamental understanding of two-phase reacting flows, and development of a database for validation of spray combustion models being developed by JPL, Sandia-Livermore, and Los Alamos National Laboratories. The most important application is in the area of alternative fuels, where their efficient utilization demands predictive correlations between the operating variables (nozzle design, swirl, and air/fuel ratio for any given fuel) and the resulting combustion characteristics, especially combustion efficiency and formation of pollutants.

During the current year, important advances have been made in three areas: (i) elucidation of the effect of fuel chemistry on spray combustion, (ii) development of a time-resolved technique for measurement of droplet sizes in sprays, and (iii) comparison of three different droplet sizing techniques. In the first area, major emphasis has been on studies of fuel mixtures. Experiments with spray flames fueled by pure methanol, as well as methanol/dodecanol mixtures, have been carried out with a phase/Doppler droplet sizing instrument. Evidence of the occurrence of micro-explosions of vaporizing droplets, predicted earlier for such binary fuel mixtures, was obtained in spray flames. The result is important, because such secondary atomization processes could have a significant impact on improving combustion efficiency. In a parallel effort, measurements on methanol/toluene mixture flames were made for the purpose of studying sooting characteristics. A light-intensity deconvolution instrument was used to generate droplet-diameter profiles of several single-component and bi-component fuels. In the second area, the polarization-ratio technique for measurement of droplet diameters in sprays has been extended to allow time-resolved data acquisition. The new technique has been used to elucidate the temporal variation of droplet sizes and concentrations in steady sprays. In the third area, a comparative analysis was carried out between the phase/Doppler, light-intensity deconvolution, and polarization-ratio techniques. The results reveal a selective sensitivity of each technique to different ranges of droplet size.

In addition to the above activities, we plan to initiate a study, in cooperation with Cornell University, to investigate the combustion characteristics of hazardous-waste liquids with varying water content. The work is expected to begin in FY92.

5. Single-Droplet Diagnostics and Modelling

J.T. Hodges, H.G. Semerjian, C. Megaridis (Univ. Illinois at Chicago), and G. Grehan (Univ. Rouen)

Both diesel and direct injection internal combustion engines, as well as gas turbines and industrial furnaces, rely on fuel injection and its subsequent mixing with the gas phase oxidant to produce a combustible mixture. Liquid vaporization and mixing processes influence the combustion event to a significant extent. For these reasons, liquid droplet/gas phase interactions are of importance in the understanding of many combustion systems. A new project has been initiated in the Process Measurements Division, including both experimental and modelling studies in single fuel droplets.

The experimental studies will be conducted on levitated droplets. The experimental apparatus for that purpose is currently being set up. An electrodynamic balance has been constructed and is operational. A servo system for balancing the droplet under conditions of changing size has been designed, which will be necessary to stabilize the droplet within the balance under conditions of rapid evaporation. A droplet generation system is also being assembled so that droplets of a known nominal size can be generated on demand. A long-distance microscope, coupled to an intensified CCD array, will provide high resolution (2 μm) high magnification imaging of the suspended drops. This apparatus will also be utilized for direct validation of the generalized Mie theory for scattering of non-planar waves being developed at the University of Rouen, as part of a NATO funded collaborative project.

The apparatus will allow observation of levitated spherical droplets under conditions of controlled temperature and convective flow field. Droplets will be electrostatically charged and suspended in the electrodynamic balance, which will provide independent control of initial size, composition, flow velocity and temperature. Droplet diameters will range from 10 to 200 μm. The size will be determined by measuring the angular distribution of elastic scattering. Rates of evaporation will be measured via the time dependence of particle size. In the case of some binary and tertiary mixtures, the composition can be determined from Raman scattering. Internal mixing processes within the droplet will be studied using a laser-induced fluorescence technique. We will also attempt to quantify the relationship between the fluorescence signal and droplet mass. This information will be valuable for those using such fluorescence techniques to quantify droplet mass concentration in real sprays. Internal mixing of the droplet will be observed via high magnification imaging of fluorescing droplets. Such 2D imaging will provide some data needed to validate models of internal mixing and diffusion within droplets.

In addition, a model of single-particle processes, including such details as internal circulation and multicomponent liquid vaporization, has been developed in collaboration with the University of Illinois at Chicago. For comparison with our recent experimental studies in spray flames (see previous report), the model has been applied to combustion of droplets consisting of methanol-dodecanol mixtures.

6. Destruction of Organic Compounds in Fluidized-Bed Reactors

A. Maček, S.R. Charagundla, C.T. Avedisian (Cornell Univ.), Y.D. Chung (Cornell Univ.), and N. Quick (EG&G Rocky Flats)

The overall objective of the high-temperature fluidized-bed studies is the understanding of combustion and pyrolysis phenomena associated with the processing of industrial fuels. While early efforts were devoted to combustion of coal particles, the primary thrust of current studies is the destruction of hazardous wastes, a topic of major national concern. During the past year, major advances have been made toward identification and measurement of intermediates formed during oxidative destruction of model compounds, and of chemical reaction rates associated with these species. In addition, new projects have been initiated on (i) destruction of solid waste ingredients and (ii) corrosion/erosion of structural materials in fluidized media.

Destruction studies of three organic model compounds -- propane, methyl chloride, and trichloroethylene -- have been completed up to about 800 °C in air. On-line FTIR analysis was performed on the model compounds and their reaction products, both intermediate and final. In the case of propane, the large amounts of carbon monoxide formed at relatively low temperatures are adequately destroyed at higher temperatures. However, the oxidation of this intermediate is severely retarded in the case of chlorinated compounds, which is in qualitative agreement with the known behavior in single-phase gaseous media. It has also been demonstrated that several chlorine-containing products of incomplete combustion form and persist up to the highest temperatures of these tests. This is significant because some of these intermediates, notably phosgene and methylene chloride, are at least as toxic as the original model compounds. In addition, global kinetic expressions have been obtained for oxidative destruction of the three model compounds.

A new project has been initiated, as part of a cooperative effort with Cornell University, on destruction of municipal solid-waste ingredients in fluidized beds. Polymethyl methacrylate particles were injected into the bed at elevated temperatures. The operation of the FTIR spectrometer was modified to allow repetitive scanning of spectra at 0.89 Hz. Thus, time-resolved analysis could be performed on the products, both pyrolytic and oxidative, that are released by the bed. These studies are continuing. Another cooperative project, with EG&G Rocky Flats, is under way to investigate corrosion/erosion characteristics of materials in high-temperature fluidized media. Exposure of several metal and ceramic samples to chlorine-containing fluidized environments at 700 °C has yielded results that show promise for the development of accelerated life-time testing of structural materials.

7. Materials Synthesis in High Temperature Reacting Flows

M.R. Zachariah, S.M. Huzarewicz, and E. Blaisten-Barojas (Johns Hopkins Univ.)

The overall objective of this project is to examine the dynamics of vapor-phase formation and growth of particles in high temperature processes. The primary effort has focussed on the use of gas phase combustion as an industrially promising reaction media for particle synthesis. The goals of the research effort are to develop:

- new methods for the synthesis of materials with novel or highly desirable properties (i.e., size, morphology, chemical composition);
- *in-situ*, optically based measurement schemes that may have applicability to on-line process monitoring; and
- molecular-level models for chemical kinetics and nucleation which can be used for optimization of ceramic and semiconductor particle processing.

As an example of a new synthesis scheme, we have demonstrated the ability to produce submicron powders of the high T_c superconductor YBaCuO via aerosol synthesis in a flame. The results of this study have shown the effects of reactor geometry, flame configuration, and temperature on particle morphology and superconducting characteristics. Materials of a solid, submicron, unagglomerated nature, with transition temperatures of 92 K, were obtained under optimal conditions.

During the past year, we also have continued development of a detailed chemical kinetic model for silane oxidation and pyrolysis leading to particle formation. The model is being tested against our previous *in-situ* measurements of particle size, number density, and species concentration profiles in a hydrogen/oxygen counter-flow diffusion flame doped with silane. At the present time we have identified the most likely chemical pathways and the most important nucleating species. This Si-O growth mechanism is relevant to the formation of high purity optical materials, e.g., optical fibers. In addition, this mechanism has been incorporated into a chemical vapor deposition/particle nucleation code being developed at the Hitachi Corporation.

A significant new direction for understanding high temperature materials synthesis has been realized this year with the completion of a study on the dynamics and mechanism of energy accommodation during cluster-cluster collisions. Simulations, carried out using a molecular dynamics approach and a realistic Si-Si interaction potential, show the silicon clusters to have the appropriate liquid-like behavior expected for these temperatures (1800 K). In cluster-cluster collisions, the collision energy is rapidly redistributed into a lower configurational energy resulting in the formation of a more stable, larger cluster. These results explain the observed high chemical reactivity of clusters and validate previous assumptions used in aerosol dynamic models which assume unity sticking coefficients. In the future, the molecular dynamics simulations will be extended to charged clusters and to cluster-surface interactions. These simulations will be directed toward issues of importance to the micro-electronics community, including cluster and particle growth in plasma etching reactors as well as cluster enhanced CVD processes.

In the coming year, a major effort will be directed toward the completion of a new laboratory and the construction and testing of a high temperature flow reactor with molecular-beam mass spectrometry sampling. This reactor will provide a new capability to precisely control high temperature chemical processes and simultaneously use a wide variety of diagnostic methods to accurately determine elementary reaction steps and rates important to the formation of particles and thin films.

8. Numerical Modelling of Reacting Flows: Semiconductor Processing and Diffusion Flames

R.W. Davis, E.F. Moore, M.R. Zachariah, D.R. Burgess, W. Tsang (833), W.G. Mallard (833), W.M. Roquemore (WRDC), and L.D. Chen (Univ. Iowa)

Over the past several years, our numerical model for a low-speed axisymmetric jet diffusion flame has consistently produced results that are in excellent agreement with the experimental observations made as part of a collaborative program with Wright Research and Development Center (WRDC) and the University of Iowa. This past year has resulted in another significant success for the model. A previously unknown phenomenon, recently observed experimentally, has also been observed in the numerical simulations. This phenomenon is the sudden jumps in flame flicker frequency that occur at certain discrete values of air coflow velocity. These frequency jumps or transitions occur at very similar values of coflow velocity, whether they are determined numerically or experimentally. Their origin is not presently understood, but it could be related to chaotic dynamics.

A significant enhancement to the computational code for axisymmetric unsteady diffusion flames has been realized this year. In the latest version, new outflow boundary conditions and the assumption of no upstream feedback allow the calculation to be restricted to only the lower flame region, thus greatly improving computational efficiency. As a result, flames in much higher speed flows, with velocities of 5-10 m/s (at least a ten-fold increase over the previous code), can now be calculated. This will permit the modeling of "transitional" jet diffusion flames, i.e., flames approaching turbulent transition but still laminar in their base regions. An important advance has thus been made toward our ultimate objective of simulating the practical types of high-speed flames that occur in industrial processes. With support from WRDC, we will generate the first numerical results from this new code for comparison with experiments.

In the past year, we have initiated a study of fluid flows in systems representative of Chemical Vapor Deposition (CVD) reactors. The first effort involves an axisymmetric flow model for a pedestal CVD reactor. Preliminary results for velocity profiles and temperature have compared very favorably with experimental measurements provided by Sandia National Laboratories. A new thrust for the coming year will involve the study of the fate of particles that form in, or are injected into, this CVD reactor. Results of this study will bear directly on the wide-spread problem of particulate contamination of CVD films.

The development of reliable reactor models, which incorporate both the chemistry and transport processes, is necessary for optimization and control of CVD systems. A major stumbling block to the development of such reactor models is that the inclusion of detailed chemistry coupled with fluid dynamics requires computational capabilities that exceed those of the state-of-the-art machines. Even a simple chemical system may involve 10-15 species and 50-100 or more reactions. Different subsets of these may be important at different points in the flow due to variations in the temperature and concentration fields. Many reactions can be eliminated by testing the sensitivity of the system to the chemistry (both kinetic and thermodynamic), over the range of concentrations and temperatures (and their gradients) that are characteristic of the reactor. However, for these complex chemical systems, which can be treated only by means of large scale numerical calculations, this is often prohibitively time consuming. To overcome this technical bottleneck, we have developed an interactive, graphics-based, post-processor for numerical simulations of chemical kinetics. It allows one to rapidly sort through and display information about species and reactions generated in the numerical simulations. We have also developed an interactive, 3-D color graphics package for visualizing the results of large-scale computer simulations and facilitating identification of correlations in highly coupled systems. Such interactive graphical analyses enable the development of a fundamental understanding of complex coupled systems through the ability to quickly probe the impact of process parameters and proposed mechanisms.

During the past year, we employed these new analysis tools to study the coupled chemistry and transport in a model system: silane decomposition leading to silicon deposition. We have shown that this system, with roughly 15 species and 40 reactions, can be reduced to only 5 species and 5 reactions, which are kinetically independent under a wide variety of temperature and concentration fields. This simplified, reduced-mechanism is possible because we now know, via our graphics-based analysis, that the concentrations of many species are at steady state, and many reactions are at equilibrium. This simplification has been included in a solution to the problem of the deposition of the reactive gas flowing over a heated substrate. The gas phase concentration profiles and the calculated silicon deposition rate were the same whether the reduced or the full mechanism was used. With the visualization package, the calculated spatial profiles of temperature, velocity, and species concentrations in the hot-wall CVD reactor can be simultaneously presented. This has been very valuable in identifying simplifying relationships, and in developing a basic understanding of the complex coupling between mass/heat transport and chemical processes.

9. Optical Diagnostics in Chemically Reacting Flows

R.J. Joklik, W.S. Hurst, G.J. Rosasco, W.J. Bowers, S. Green (NASA Goddard), L.A. Rahn (Sandia Nat. Lab.-Livermore), and R.A. Farrow (Sandia Nat. Lab.-Livermore)

The recently developed high resolution CARS spectrometer system, described in last year's report, has been applied in a successful experimental validation of the first *ab initio* calculation of the pressure induced collapse of the spectrum of CO. This is the first time that CARS spectra have been measured with sufficient accuracy to enable a detailed comparison to fundamental theory. In this study, the shapes of nearly isolated lines at sub-atmospheric pressures were shown to agree with theory to 1%. The theory also includes the phenomenon of collisional collapse, in which the multi-line Q branch narrows to a nearly continuous distribution that approaches a single-line spectrum. The agreement of experiment and theory for the collapsed spectrum was generally within 2%. This work, in collaboration with NASA Goddard, demonstrates the accuracy of the physical model that underlies the use of the CARS spectra of molecules like N_2 and CO for temperature and pressure measurements in reacting flows.

The temperature dependence of the line broadening coefficients of the Q-branch transitions of pure H_2 were measured and analyzed as part of our continuing collaboration with Sandia National Laboratories. An energy-corrected sudden scaling law, which included rotation-to-rotation energy exchange as well as the more familiar rotation-to-translation energy exchange, accounted for all the rotational state (J) and temperature (T) dependence of the line broadening. This work has provided the first accurate, physically motivated procedure for predicting the temperature dependence of the H_2 spectrum. The spectrum of H_2 has great appeal for diagnostic applications. It is strong, allowing detection at very low concentrations and, if the linewidths are known, can be used as a temperature diagnostic. Perhaps more important, as we have previously demonstrated, it can be used to simultaneously provide a measurement of pressure. This area of investigation will be expanded to include the D_2:Ar system, our proposed primary standard for transient pressure and temperature.

Our efforts to develop the Thermally Assisted laser induced Fluorescence (THAF) technique as a reliable temperature measurement approach for flames and combustors has continued during the past year. We have shown that THAF measurements, based on the molecular species OH and single-shot temperature measurements, yield 5% accuracy for a wide range of fuel-rich and fuel-lean conditions in methane, acetylene, and ethylene flames. These measurements have been validated by both Na line reversal and OH rotational temperature measurements for flames with temperatures from 1500 to 2700 K. This capability is of interest for jet engine diagnostics and for this purpose a fiber-optics based measurement system, with a single point-of-access, has been designed and demonstrated. Work during the coming year is expected to involve calibration of the OH-THAF spectrum for a prototypical jet fuel, and an investigation of the use of an approach to temperature measurement based on the resolved spectrum of the fluorescence from (0-1) and (1-2) vibrational bands. The latter has a special appeal in that it may provide a more robust calibration method, independent of the experimental system.

10. Development of a Dynamic Pressure and Temperature Primary Standard

V.E. Bean, W.S. Hurst, W.J. Bowers, and G.J. Rosasco

A Workshop on the Measurement of Transient Pressure and Temperature was held at NIST in April 1991 to identify current and emerging measurement problems and needs, identify scientific and technical barriers and opportunities to achieving measurement accuracy goals, and to assist in the formulation of an appropriate role for NIST. The workshop attracted almost eighty attendees from government laboratories, private sector laboratories, and instrumentation manufacturers; these included attendees from six foreign nations. Twelve technical talks were presented which focused on measurement needs and various ways of meeting these needs. A common thread in these presentations and the associated discussion was the need for traceability to national standards that is currently unavailable. The most significant points that emerged from the discussions can be summarized as follows:

- NIST should develop standards to provide traceability for the calibration of transient pressure transducers.

- The attendees were generally willing to collaborate in solving measurement problems, both through a working group organized to provide a forum for discussion and through measurement round-robins.

- The shock tube is the method of choice for obtaining pressure transducer transfer functions because of the fast rise time and "known" shape of the pressure pulse.

- There was genuine interest in the NIST proposal to develop a national standard based on transfer of a molecular-level primary standard to a reference shock tube.

During the past year, we have taken a number of steps toward realization of a national standard for transient temperature and pressure. First, an effort was initiated to modify a shock tube (previously obtained from the Naval Research Laboratory) to increase its pressure range to 20 MPa. The modifications to the design have been safety-certified by a licensed professional engineer. In addition to conventional instrumentation, the shock tube will have windows for optical diagnostics. We expect to begin testing the shock tube early in the FY92.

This shock tube will be the pressure generator for the testing of transient pressure transducers and the reference source for the round-robins suggested by the Workshop. It also will be the test-bed for our research to transfer a molecular-level primary standard for transient pressure and temperature to a reference dynamic source.

To help realize the primary, molecular-level standard, a new high pressure, high temperature optical cell for CARS spectroscopy has been developed this year. This cell is compatible with hydrogen and is capable of operating at pressures up to 100 MPa at 1000 K. In the coming year a systematic study of the temperature and pressure dependence of the Raman Q-branch spectrum of D_2 in Ar will be performed to provide the data-base for transient pressure and temperature calibrations. In preparation for this study, high-quality spectra of this system recently have been obtained using the new high resolution CARS spectrometer (see previous report).

11. Oxidation in Supercritical Water Flow-Reactors

G.J. Rosasco, A. Macek, J.M.H.L. Sengers (838), V.E. Bean, S.R. Charagundla, W.J. Bowers, W. Tsang (833), and D.R. Burgess

A new research effort was initiated in the past year to provide understanding, process models, and engineering data in support of the development of SuperCritical Water Oxidation (SCWO) as a safe and efficient process for disposal of industrial wastes. Among the technical barriers to industrial utilization of this promising technology is the lack of reliable process models which provide a basis for reactor design, selection of operating conditions, and prediction of process efficiency. These process models require information on phase, chemical species, and chemical reactions for the pressure and temperature conditions of supercritical water. Additionally, data on the performance of the materials of construction for an industrial reactor must be provided.

To help provide the needed data, we are constructing two laboratory-scale supercritical water flow-reactors. The first of these reactors provides optical access to allow *in-situ* optical measurements of fluid phase, chemical species, and reaction intermediates and products. Initial experiments will involve measurements of density and composition as functions of temperature, pressure, and solute concentration for model ammonium compounds. In addition to the optically accessible flow system, a flow reactor for complementary studies of global kinetics, reactor-material durability, and process efficiency has been designed. This system will have a complement of analytical instrumentation for detailed studies of input-reactant and total end-product (including materials degradation products). Construction has begun, and these systems should be operational in early FY92.

In parallel with the development of these experimental systems, some preliminary explorations of reaction kinetics have been carried out in the past year. Most of the fundamental reactions that are thought to be important to oxidation in supercritical water are common to atmospheric pressure combustion. The observation of unusually high destruction efficiencies found in the supercritical water environment has led to questions with respect to microscopic mechanisms and fundamental rates, even for what might be expected to be a well understood process, e.g., the oxidation of CO. Analysis of the proposed microscopic multi-step mechanism (with more than 60 elementary reactions) for this process, using our recently developed graphics based post-processor, has revealed a number of key steps that must be evaluated to validate the model. One such reaction of special fundamental interest is the elementary water-gas shift reaction in a high density water environment. An experimental test has been proposed which utilizes the new high pressure shock tube facility being developed for transient pressure calibrations. Another important result of the modelling is the suggestion that heterogeneous (wall) reactions act as an ignition source in the supercritical reactor. Fundamental questions of this sort are expected to be widely encountered as we continue the study and evaluation of this promising new technology.

12. Ultrathin-Film Chemical Sensors

S. Semancik, R.E. Cavicchi, J. Vetrone (Northwestern Univ.), and Y.W. Chung (Northwestern Univ.)

The production of reliable solid state chemical sensing devices depends critically on the development of improved transducer materials. At present, most commercially available solid state gas sensors are based on sintered powder forms of tin oxide (SnO_2) and other oxides. To create sensors with stable, fast and reproducible response characteristics, one must tailor the active materials so they not only have acceptable electronic characteristics, but also interact with the chemical environment (gas or solution) in a simple way. Previous work in this project has indicated that model sensors fabricated from SnO_2 single crystals can meet both of these requirements. In addition, we have demonstrated how surface phenomena can dominate the detection process, and how this fact can be used to advantage in developing next-generation sensors. Because of their high cost, however, SnO_2 single crystals are generally not practical as sensor elements. Therefore, we have investigated the formation of thin film forms of base sensor materials such as SnO_2 that emulate the degree of order found in single crystals. Heteroepitaxial films, fabricated on commercially viable single crystal substrates such as sapphire (already widely used for silicon-on-sapphire technology and for high temperature superconductors), are expected to play a primary role in future sensor production, especially in sensor arrays that will analyze multicomponent mixtures.

Fabrication, characterization and response testing at NIST have been performed in newly consolidated laboratories that house our multi-technique surface analytical facility as well as our ultrahigh vacuum-based deposition facility. During FY91, we were successful in producing epitaxial SnO_2 on single crystal substrates including TiO_2(110), sapphire(0001) and sapphire(1102). Depositions were carried out at elevated temperatures using low-rate, reactive sputter deposition. X-ray diffraction indicates that the 200-2500Å films formed are oriented (110), (100) and (101), respectively, on these substrates, and low energy electron diffraction indicates that the highly-ordered structure extends to the surfaces of the films. Scanning electron microscopy and atomic force microscopy (through a collaboration with the University of Maine) have shown that the films are extremely smooth (rms roughness over $1mm^2$ ranging from 2-20Å), and their purity, order and smoothness may make them important in technological areas other than sensing (e.g., optical coatings, low friction coatings, etc.). The growth of epitaxial SnO_2 films on insulating sapphire (patent pending), however, is particularly significant for producing integrated sensor arrays. While the efforts at NIST have focused on reactive sputter deposition of SnO_2, organometallic chemical vapor deposition (OMCVD) has also been studied as part of a cooperative agreement with Northwestern University. Analyses of the OMCVD films at NIST showed that while they are similar in stoichiometry, they do not exhibit as high a level of smoothness or structural order.

Deposition of overlayer metals in the coverage range of 0.1 to 10 monolayer equivalents (ML) was studied to understand the electronic effects that occur for surface-dispersed, selectivity-enhancing additives. Real time effects of the interaction of the dispersed metals with the oxide support were examined using surface conductance and surface spectroscopic techniques. Following deposition of 3 ML of Pd on $SnO_2(110)$ crystals and various SnO_2 films, conductance response characteristics were measured to cycles of H_2, O_2, CO and H_2 in dry and humidified air. While the gas sensing response for single crystals, reactively sputtered films and OMCVD films are qualitatively similar, differences in response speed and stability were noted and are the subject of continued studies. Development of automated testing equipment is underway for these and other systematic investigations.

In a related effort, the feasibility of a new gas sensing structure based on diode characteristics has been shown using single crystal TiO_2 and metallic contacts. The rectifying behavior of this structure shows high sensitivity to gas exposure ranging from strong rectification to ohmic characteristics.

Microstructural properties are expected to be responsible for some of the response differences between thin film and single crystal sensors. We will continue to examine microstructural effects for Pd/SnO_2 and other metal/oxide systems (e.g., Ag or Cu on TiO_2 or ZnO) and their influences on sensing behavior. With the addition of a scanning tunneling microscope (STM) to our surface analytical facility, we will be able to obtain more detailed information on the structure of additives at such interfaces.

13. Characterization of Plasma Processing Reactors

J.R. Whetstone, M.A. Sobolewski, J. Olthoff (EEEL), R. Van Brunt (EEEL), and J. Roberts (PL)

This is a collaborative area of research between the Process Measurements Division and two other NIST laboratories, EEEL and PL. Plasma processes of interest are those used in pattern transfer processes necessary for semiconductor device fabrication. Achievement of submicron feature sizes relies solely upon the plasma etching of silicon and SiO_2. Most plasma reactors are based on radio frequency (RF) excited plasmas, and employ a range of chemistries to achieve the desired pattern transfer characteristics, e.g., high aspect ratio trenches necessary in high-density dynamic random access memory cells. Process control requirements in process tools are becoming more stringent as device feature sizes decrease and wafer processing times are reduced. Improvements in the areas of process control techniques, characterization of the physical and chemical properties of the plasma, and reliable process models are needed as a basis for future reactor design methods.

Activities this year have centered on characterization of various aspects of a standard discharge cell geometry, the GEC (Gaseous Electronics Conference) reference discharge cell. GEC discharge cells have been assembled and operated in several research laboratories with the intent of determining and improving the comparability level of basic measurement results. Initial measurements have been made at five laboratories: Sandia National Labs, AT&T Bell Labs, Wright-Patterson Air Force Base, Univ. of New Mexico and NIST. These involve the major plasma discharge cell operating parameters, RF power dissipated in the plasma determined from voltage and current measurements at the cell electrodes as a function of operating pressures, gas flow rates. Comparative measurements were performed by the participating laboratories and the results were presented at the 1990 GEC. Intimately connected with these measurements is an equivalent circuit model necessary to relate the measurements made outside the cell to values of voltage and current in the plasma itself. NIST has extended the initial model proposed by Sandia to obtain more accurate plasma voltage and current values. These techniques have been used in conjunction with simultaneous optical emission and mass spectrometric measurements to investigate behavior of plasma electrons and ions to further characterize operation of the GEC reference discharge cell. These results and characterization methods are applicable to the many types of plasma reactors normally used in the manufacture of integrated circuits.

In the coming year, a second GEC reference cell will be put into operation in the Division's Optical Diagnostics Laboratory. The concentrations of several species will be measured under well-characterized operating conditions, in typical reactive etchant gases, using both LIF and optical emission techniques. Introduction of silicon is planned to study a variety of process monitoring methods.

14. Self-Assembled Organic Monomolecular Films

M.J. Tarlov and E. Bowden (North Carolina State Univ.)

Self-assembled monolayers (SAMs) formed spontaneously by the immersion of an appropriate substrate in a surfactant solution are being investigated for their potential as chemical sensing elements. SAMs comprised of alkanethiols chemisorbed on gold are particularly attractive in this regard because they form densely packed, ordered molecular arrays where the exposed surface organic functional group can be easily controlled. Such surfaces are ideal systems for the construction and study of highly selective, molecular recognition type sensors for chemical and biotechnological applications. In addition, there are many exciting possibilities for using SAMs as adhesion layers, corrosion barriers, and elements in molecular and opto-electronic devices.

In many chemical sensing applications, well-defined organic multilayer structures would have great utility. In this regard, we have been investigating the deposition of metals on methyl-terminated SAMs as a possible method to construct multilayers. Here the metal overlayer would serve as a substrate for the assembly of another organic monolayer. We have extensively examined the deposition of Ag on alkanethiol monolayers self-assembled on Au using photoelectron spectroscopies (x-ray, ultraviolet and infrared) and ion scattering spectroscopy. Surprisingly, our results indicate that Ag penetrates the monolayer and forms clusters at the SAM/Au interface when vapor deposited on a SAM/Au sample is held at room temperature. Remarkably, the structural integrity of the SAM is largely maintained during the process. The Ag can be made to stay on top of the SAM if the deposition is performed at 90 K; however, this is a metastable structure because warming to room temperature results in the migration of Ag to the SAM/Au interface. Similar room temperature monolayer penetration behavior has been observed for Al and Au deposited on alkanethiol SAMs. We recently observed that an Al overlayer can be formed on top of a carboxylic acid-terminated SAM.

We are also investigating, in collaboration with the North Carolina State University, the electrochemistry of cytochrome *c* adsorbed on carboxylic acid terminated alkanethiol SAMs on gold. In this approach, cytochrome *c* is irreversibly adsorbed at near monolayer coverage on the SAM surface, and electron transfer between the gold electrode and the electroactive heme group of the protein through the SAM is monitored. The electrochemical techniques of cyclic voltammetry, impedance spectroscopy, and chronoamperometry have been used to measure the coverage, oxidation-reduction thermodynamics, and electron transfer kinetics. The electron transfer rate constant has been measured for three different SAM thicknesses (25, 16, and 9 Å) and much faster rates are observed with shorter SAM chain lengths as expected for an electron tunneling process. These studies have proved the feasibility of using SAMs to adsorb redox proteins in a native state such that direct electronic communication between a metal electrode and the protein is established. Moreover, in doing so we have demonstrated that the orientation of the adsorbed protein can be controlled by electrostatic interactions between the protein and the SAM surface. This is not only important in the construction of enzyme electrodes, but also could impact other fields such as bioseparations and biosynthesis.

Future directions include examination of the ion-exchange behavior of carboxylic acid-terminated SAMs. Preliminary results indicate that transition metal cations can be adsorbed from solution on carboxylic acid-terminated surfaces. In collaboration with the Biotechnology Division, we also plan to examine the self-assembly of biotin containing monolayers which could be used for biotin-avidin coupling reactions. The success of this project would permit the facile construction of a wide range of highly selective, ultrafast, miniature, enzyme-selective electrodes.

15. Thin-Film Thermocouples and Thermocouple Materials

K.G. Kreider

Sputter deposition has been used to form thin-film thermocouples for several applications. These structures, placed in a diesel engine combustion chamber, provide the means for making temperature measurements during the combustion process on each engine stroke. Both average and transient response of the thermocouple are of interest. The NIST effort is an outgrowth of work on thin-film thermocouples for application to a variety of high temperature, harsh environment processes. Currently, sensor plugs for the DoE/Cummins Heavy Duty Diesel Engine project are prepared with thin-film thermocouples on their surface. These plugs replace one of the four valves in the engine, providing a non-intrusive method for measuring combustion temperature. These thermocouples have been calibrated and evaluated for durability in air at up to 1200 K in our laboratory. The sensor plugs are used to evaluate ceramic-lined diesel engines and uniquely provide the fast response needed for *in-situ*, instantaneous measurement of heat transfer data during full power test runs.The transient response of thin-film thermocouples is also characterized using a pulsed excimer laser to deposit energy into the thermocouple structure in times much shorter (10 to 20 nanoseconds) than the temperature pulse occurring during each combustion cycle. Thermocouple response is observed using digital sampling techniques.

New types of thin-film thermocouples were fabricated including a RuO_2/IrO_2 temperature sensor which is more corrosion resistant than the best precious metal thermocouples. This new sensor should be insensitive to acids, bases, cyanides, and complexes that cause problems with biological measurements and measurements in highly corrosive solutions such as the chlor-alkali process. Additionally, transparent thin film thermocouples have been explored including those fabricated in-house from antimony tin oxide (ATO) and commercially available transparent conducting oxides. Both the in house and commercial films are excellent thermocouples with indium tin oxide (ITO). Future directions in this project include the investigation of new materials that may exhibit higher voltage output.

16. Implementation of New International Temperature Scale (ITS-90)

G.F. Strouse, E.R. Pfeiffer, G.W. Burns, G.T. Furukawa, R.S. Kaeser, and B.W. Mangum

A new International Temperature Scale (ITS-90), adopted in September 1989, came into effect in January 1990. ITS-90 has been realized in our Standard Platinum Resistance Thermometer (SPRT) Calibration Laboratory over the range 83.8 to 1337.3 K. However, until the new NIST facilities for realizing the ITS-90 and for calibrating customer thermometers below 83.8 K are completed, a continuing concern is the maintenance and stability of the present low-temperature scale, which serves as the NIST reference for calibrations in the region 0.65 K to 83.8 K. The NIST-ITS-90 reference scale actually consists of two distinct "wire scales": an SPRT-based scale spanning the region 13.8 K to 83.8 K, used primarily for calibration of SPRTs, and a Rhodium-Iron Resistance Thermometer (RIRT) based scale spanning the region 0.65 K to 27.1 K, used primarily for calibration of RIRTs and Germanium Resistance Thermometers (GRTs). In FY91, three additional SPRTs and one RIRT were calibrated to serve as backup thermometers to insure continued maintenance of the NIST reference scale. In addition, the main SPRT and RIRT reference sensors for NIST-ITS-90 were intercompared again over their common region (13.8 K to 27.1 K) in a continuing investigation of the long-term stability of the RIRTs. All SPRT comparisons include measurements at the NIST-ITS-90 calibration points, as well as measurements at selected intermediate points, to accumulate data regarding the non-uniqueness of SPRT-indicated T_{90} values between the calibration points.

Some additional upgrades were made this year in the SPRT Calibration Laboratory where calibrations above 83 K are performed. A new protection system for holding high-temperature SPRTs (HTSPRTs) was constructed and installed in pre-heat furnaces that are used to heat HTSPRTs to temperatures above 500 °C. This was required since metal ions readily diffuse through the silica glass sheaths of HTSPRTs at high temperatures, degrading the Pt sensor through alloying. This system, which has been shown at NIST and elsewhere to adequately protect the HTSPRTs, consists of a thin-wall platinum tube sandwiched between two silica-glass tubes.

There are no systematic data on the non-uniqueness of temperature values of HTSPRTs in the range 631 °C to 962 °C, and such data are also sparse in the range 20 °C to 630 °C at the levels of precision that can be achieved with modern measurement equipment; therefore, precise comparison data are urgently needed to determine the limitations of the ITS-90. To determine the non-uniqueness, the temperature uniformity and temperature stability of the comparison apparatus must be at least as good as the measurement precision. For this work, two metal-block comparison apparatuses are being assembled, one for operation between about 400 °C and 1000 °C and the other between about 20 °C and 600 °C. To achieve the desired thermal uniformity and stability, a system of multiple thermal shields is used. The higher temperature apparatus is designed for 7 SPRTs, the lower temperature one for 9 SPRTs, of which 3 could be capsule SPRTs in holders. The apparatuses will be used in the future for automatic comparison calibrations.

For the 400 °C to 1000 °C comparison apparatus, the comparison block, thermal shield parts, and thermometer wells, which will be at temperatures as high as 1000 °C, have been constructed of Inconel alloy for its high-temperature stability. A sealed heat pipe using potassium is the outer thermal shield. This comparator is complete except for a few refinements. The comparison block and the thermal shields of the second apparatus were constructed of copper for its high thermal conductivity. Since copper readily oxidizes and loses its thermal reflectivity, the comparison block and the copper shields have sheet silver covers on the surfaces. Additional sheet-silver thermal shields are also used to reduce the electric power requirements. The comparator system will be operated in vacuum. The parts of this comparator have been constructed and it and the electronic temperature control system are ready to be assembled and tested.

The Liquid-in-Glass Thermometry Laboratory was upgraded this year by the purchase of a temperature-controlled oil bath (100 °C to 300 °C) that is to replace two manually-controlled oil baths, and by putting into operation two new temperature-controlled liquid baths, one water and one salt. The water bath replaced a manually-controlled water bath (0 °C to 100 °C) and the salt bath replaced a manually-controlled molten-tin bath (300 °C to 550 °C). Prior to putting the water and salt baths into service, they were evaluated and their operations were found to be excellent. The new oil bath has been received recently and it will be put into service after evaluation.

17. Realization of ITS-90 below 84 K

M.L. Reilly, C.W. Meyer, W.E. Fogle, and B.W. Mangum

The new NIST facility for the primary realization of the ITS-90 below 25 K is under development. This facility will serve a two-fold purpose; first, it will be used to realize the ITS-90 between 0.65 K and 24.56 K, as defined, with an inaccuracy not greater than 0.1 mK, and to provide primary calibrations for capsule-type SPRTs and RIRTs which subsequently will be used to transfer the ITS-90 to the NIST user community. The realization of the ITS-90 below 25 K requires realizing the six fixed points of this range and developing a significant new instrumentation and measurement capability, particularly for vapor-pressure thermometry of ^{3}He and ^{4}He and for interpolating constant-volume gas thermometry employing either ^{3}He or ^{4}He. Neither of the latter techniques was used to realize the IPTS-68. The second purpose of the facility will be to investigate and document the non-uniqueness of the ITS-90 that is associated with the overlapping definitions of the scale in the range below 25 K as well as the inherent performance differences of the individual scale-defining instruments. The goal is to have the facility fully operational by the end of FY92.

During FY91, the modification of the laboratory for the facility was completed. The ^{3}He refrigerator was assembled and preliminary runs at liquid N_2 and liquid ^{4}He temperatures were conducted. The design of the refrigerator insert, which contains the interpolating constant-volume gas thermometer bulb, the bulbs for the vapor-pressure fixed points, and the bulbs for the triple-point fixed points, is nearing completion; its construction will begin in FY92.

The performance of the piston gage, which will be used to measure the pressures required to realize four of the six fixed points below 25 K, was characterized through an experiment designed to measure the ratios A_x/A_{N_2}, where A_x is the "effective area" of the piston for ^{3}He, ^{4}He, or H_2 and A_{N_2} is the "effective area" of the piston as calibrated with N_2. The ratios A_x/A_{N_2} were determined over the pressure range 0.02 to approximately 1 standard atmosphere. Values of A_x were found to differ from A_{N_2} by as much as 20 ppm, which is significant in the realization of fixed points with an inaccuracy of 0.1 mK or less.

This year plans and specifications were formulated for a new ^{3}He refrigerator for the ITS-90 facility for realization of the scale between 13.8 K and 84 K and for calibration over the range 0.65 K and 84 K. Assembly of the new facility will start during FY92. Substantial progress has also been made on an effort to examine the accuracy of the ITS-90 at its low end. An experiment to measure the susceptibility of an empty copper-coil set has been completed. In the second stage of this effort, which is underway, this coil set will be used to examine the temperature dependence (based on the ITS-90) of the susceptibility of cerous magnesium nitrate powder. An analysis of the results, in terms of a Curie Law temperature dependence, will serve to test the internal consistency of the temperature scale above versus below 1 K.

18. High Temperature Thermometry Research

G.W. Burns, M.G. Scroger, G.F. Strouse, B.M. Liu, and B.W. Mangum

Work in this area is concerned with thermocouples (TCs) and SPRTs. Studies of the emf stability and repeatability of Au/Pt TCs with prolonged heating at or near the freezing point of Ag (961.78 °C) and after rapid thermal cycling between the Ag point and room temperature were continued. The time of heating of one Au/Pt TC at the Ag point was extended to 1200 hours and the number of thermal cycles of the TC to room temperature was increased to 142. No discernible change ($\leq$15 mK) was detected in the emf of the TC at the Ag point as a result of these thermal treatments.

An experiment (part of an international effort, coordinated and evaluated by NIST) for determining the emf-t_{90} relationships of a group of Type S, Type R, Type B, Au/Pt, and Pt/Pd TCs over the range from -50 °C to 1070 °C (1000 °C for Au/Pt) was designed and carried out to obtain experimental data for establishing new reference functions and tables for these TC types based on the ITS-90.

experiment. All of the TCs were fabricated from 0.5 mm diameter wires that were given special annealing treatments and were then assembled in high-purity alumina insulating tubes. Additionally, all the TC assemblies were given special heat treatments in a laboratory furnace both before and during the experiment to enhance their performances. In this experiment the TCs were compared with SPRTs and HTSPRTs that were calibrated according to the ITS-90 to 962 °C, with an extrapolation to 1070 °C. Comparison measurements were made in a cryostat below 0 °C, in stirred liquid baths in the range 0 °C to 550 °C, and in a sodium heat pipe furnace above 550 °C. The thermoelectric voltages of the TCs were also determined at the ice point and at the freezing points of In, Sn, Cd, Zn, Al, Ag, and Au. The repeatability of the TCs was established through repetitive measurements against SPRTs or HTSPRTs and at the fixed points. The thermoelectric homogeneity of the TCs was assessed by determining their immersion characteristics in freezing-point cells.

The analyses of the experimental data obtained and derivation of the reference functions are in progress. Also, new estimates for the temperature differences between the ITS-90 and the IPTS-68 in the range 630 °C to 1064 °C have been derived from the results obtained for the Type S TCs. The results of this experiment will be reported in several papers that are to be presented at the 7th International Temperature Symposium in April 1992.

A plan for evaluation of the ITS-90, particularly at temperatures above 420 °C, through the use of HTSPRTs was developed with two other national standards laboratories (Istituto di Metrologia "G. Colonnetti" in Italy, Van Swinden Laboratory in the Netherlands). The plan involves the evaluation of 30 to 50 HTSPRTs at all fixed points from 273.16 K to 1234.93 K (from triple point of water to freezing point of Ag), and also with measurements made in the comparison furnaces described in the section "Implementation of New International Temperature Scale". Results will be used to characterize reproducibility, non-uniqueness, subrange inconsistencies, ac/dc effects, and stability of HTSPRTs. Initial calibrations and other measurements of NIST HTSPRTs to determine their non-uniqueness, reproducibility and stability have begun. HTSPRTs made at the Mendeleyev Institute of Metrology (VNIIM) were calibrated at and below the Au point temperature in order to study their reproducibility and stability, and to use them in determining temperature from 500 °C to 1064 °C in the experiments on TCs described above. Calibrations and analyses of a HTSPRT made at Physikalisch-Technische Bundesanstalt (PTB) up to 1234.93 K were also performed.

19. Thermometric Fixed Point Development

B.W. Mangum, E.R. Pfeiffer, G.T. Furukawa, G.F. Strouse, and G.W. Burns

The certification of SRM 740A (Zinc Freezing-Point Standard) was completed this year. The 99.9999+% pure Zn was in the form of millimeter-size "shot". The 200 gram units are packaged in plastic envelopes with an argon atmosphere.

Two new Ag freezing-point (961.78 °C) cells were constructed from source material consisting of commercial 99.9999+% pure shot; an evaluation of the cells has begun. Preliminary tests of melting and freezing behavior of the first of these cells indicate that its freezing-point temperature is lower than that of our reference Ag cell by several mK. This is attributed to the possible presence of oxygen in the cell. Tests on the second cell were initiated near the end of FY91. A new Al freezing-point (660.323 °C) cell was constructed and will be evaluated next year. The construction of a second Al cell is nearly complete. Once these four cells have been evaluated, they will serve as back-up cells for the SPRT Calibration laboratory.

Preparatory work for evaluating 99.9999+% pure Ag samples as Standard Reference Materials (SRMs) has begun. The high-purity metal sample, all of one lot, has been ordered; after a long delay, it is due to be delivered in the first quarter of FY92. Other selected materials needed to produce freezing-point cells have been obtained, and will be evaluated as potential SRMs.

SRM 1972 (ethylene carbonate) and SRM 1973 (n-docosane) are still in the production stage. Purification was initially carried out by zone-refining; since there has been a lot of breakage of zone-refining tubes during purification, a different technique is being tried. It is hoped that the materials, contained in minicells holding about 60 grams of a purified compound, will be available soon so that the SRMs can be made available to the public.

C. Outputs and Interactions (Process Measurements Division)

1. Publications

Adair, D., Madigosky, W.M., and Mease, N.E., "An Electro-optical Sensor for Surface Displacement Measurements of Compliant Coatings," Review of Scientific Instruments 62, 6 (1991).

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Cavicchi, R.E. and Semancik, S., "Reactivity of Pd and Sn Adsorbates on Plasma and Thermally Oxidized $Sn0_2(110)$," Surface Science (in press).

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2. Talks

Bean, V.E., "La Calidad y la Metrologia," The State-of-the-Art in Pressure Metrology, Mexico City, Mexico, November 27, 1990.

Bean, V.E., "Status of CCG Project 273," CCG Working Group Meeting, Newark AFB, OH, February 13, 1991.

Bean, V.E., "Dynamic Pressure and Temperature Standards," CCG Engineering Working Group Meeting, Gaithersburg, MD, February 28, 1991.

Bean, V.E., "The Development of the NIST Transient Pressure and Temperature Calibration Facility," National Conference of Standards Laboratories (NCSL) Workshop and Symposium, Albuquerque, NM, August 20, 1991.

Burgess, D.R., Jr., "Numerical Modeling of Silane Decomposition Kinetics," AIChE Annual Meeting, Chicago, IL, November 12, 1990.

Burgess, D.R., Jr., "Interactive Development of Reduced Mechanisms for Chemical Vapor Deposition," Washington Materials Forum, Washington, DC, February 28, 1991.

Burns, G.W., "Studies of New Types of Noble-Metal Thermocouples for Use as Secondary Reference Thermometers," NCSL Utilities Committee Meeting, South California Edison Company, Westminster, CA, January 30, 1991.

Cavicchi, R.E., "Investigation of the Evolution of Metal/$Sn0_2$ Interfaces Using In Situ 4-point Conductance Measurements," 51st Annual Physical Electronics Conference, Rutgers Univ., Piscataway, NJ, June 17, 1991.

Davis, R.W., "A Numerical/Experimental Study of a Buoyant Jet Diffusion Flames," 23rd Fall Technical Mtng., Eastern Section of the Combustion Institute, Orlando, FL, December 4, 1990.

Davis, R.W., "A Numerical/Experimental Study of a Buoyant Jet Diffusion Flame," Wright- Patterson Air Force Base, OH, August 19, 1991.

Davis, R.W., "A Numerical/Experimental Study of a Buoyant Jet Diffusion Flame," Space Experiments Division, NASA Lewis Research Center, Cleveland, OH, August 21, 1991.

Espina, P.I., "Fluid Flow Modeling," NIST/Industrial Consortium Meeting on Intelligent Processing of Rapidly Solidified Metal Powders by Inert Gas Atomization, NIST, Gaithersburg, MD, October 22, 1990.

Espina, P.I., "Intelligent Control of Metal Atomization: Flow Modeling," Crucible Research Metals, Pittsburgh, PA, November 2, 1990.

Espina, P.I., "Fluid Flow Modeling," NIST/Industrial Consortium Meeting on Intelligent Processing of Rapidly Solidified Metal Powders by Inert Gas Atomization, NIST, Gaithersburg, MD, December 5, 1990.

Espina, P.I., "Fluid Flow Modeling," NIST/Industrial Consortium Meeting on Intelligent Processing of Rapidly Solidified Metal Powders by Inert Gas Atomization, NIST, Gaithersburg, MD, March 21, 1991.

Espina, P.I., "Fluid Flow Modeling," NIST/Industrial Consortium Semi-Annual Meeting on Intelligent Processing of Rapidly Solidified Metal Powders by Inert Gas Atomization, NIST, Gaithersburg, MD, September 5, 1991.

Hess, D.E., "An Experimental Investigation of the Interaction of a Compliant Surface and a Turbulent Boundary Layer," Dynaflow, Inc., Laurel, MD, October 25, 1990.

Hess, D.E., "Measurements of Stable Compliant Surface Response to Bursts in a Turbulent Boundary Layer," Cornell Univ., Ithaca, NY, November 18, 1990.

Joklik, R.G., "Vibrational Thermally Assisted Laser Induced Fluorescence of $A^2\Sigma^+$OH for Temperature Measurement in Flames, 23rd Fall Technical Meeting, Eastern Section of the Combustion Institute, Orlando, FL, December 3, 1990.

Joklik, R.G., "Vibrational Thermally assisted LIF in OH for Temperature Measurement in Flames," Naval Research Lab, Washington, DC, March 19, 1991.

Kreider, K.G., "Thin Film RuO_2 and IrO_2 Thermocouples," Materials Research Society, Anaheim, CA, May 2, 1991.

Maček, A., "Oxidative Destruction of Hazardous-Waste Model Compounds in Fluidized Beds," Cornell Univ., Ithaca, NY, October 30, 1990.

Maček, A., "On-line FTIR Analysis During Fluidized-Bed Oxidation of Chlorinated Hydrocarbons," 2nd International Congress on Toxic Combustion By-Products, Univ. of Utah, Salt Lake City, UT, March 28, 1991.

Maček, A., "On-line FTIR Analysis During Fluidized-Bed Oxidation of Chlorinated Hydrocarbons," New York State Solid Waste Combustion Workshop, Cornell Univ., Ithaca, NY, April 25, 1991.

Mangum, B.W., "Standard Reference Materials and Measurement Assurance Programs for Technology Transfer, Instituto Politecnico Nacional, Mexico City, Mexico, November 26, 1990.

Mangum, B.W., "Implications of the ITS-90 for Utilities," NCSL Utilities Committee Meeting, Southern California Edison Company, Westminster, CA, January 30, 1991.

Mangum, B.W., "Practical Applications of the ITS-90: Inherent Uncertainties," 1991 Measurement Science Conference, Anaheim, CA, January 31, 1991.

Mangum, B.W., "Temperature Measurements at NIST and the New International Temperature Scale of 1990," Meeting of Region 3 Chapter of the National Conference of Standards Laboratories (NCSL), Newport News, VA, April 4, 1991.

Mangum, B.W., "Practical Applications of the ITS-90," 45th ASQC Annual Quality Congress, Milwaukee, WI, May 21, 1991.

Mattingly, G.E., "Fluid Flowrate Metrology: Laboratory Uncertainties and Traceabilities," SPIE Technical Symposium, Santa Clara, CA, October 3, 1990.

Mattingly, G.E., "Flowmeter Installation Effects: Pipeflow Measurements and Flow Conditioners," Mech. Engineering Seminar Program, Univ. of Surrey, Guildford, U.K., October 19, 1990.

Mattingly, G.E., "Effects of Pipe Elbows and Tube Bundles on 50 mm Orifice Meters, National Engineering Laboratory (NEL) Flowmeter Installation Effects Workshop, East Kilbride, Glasgow, U.K., October 22, 1990.

Mattingly, G.E., "Flowmeter Installation Effects," Mechanical Engineering Seminar Series, Univ. of Pennsylvania, Philadelphia, PA, February 7, 1991.

Mattingly, G.E., "Flow Measurement at NIST: Standards, Traceability and Related Research Programs, National Conference of Standards Laboratories (NCSL), Newport News, VA, April 4, 1991.

Mattingly, G.E., "Update on Fluid Metering Research at NIST: Installation Effects and Generic Test Results," ASME Committee Meeting on Measurement of Fluid Flow in Closed Conduits (MFFCC), New York, NY, April 11, 1991.

Mattingly, G.E., "Flow Measurement," ISA - 37th International Instrumentation Symposium, San Diego, CA, May 7, 1991.

Mattingly, G.E., "NIST Fluid Flow Calibration Technology," General Motors Corp. (Harrison Division), Lockport, NY, August 21, 1991.

Mattingly, G.E., "NIST Fluid Meter Research-Installation Effects," General Motors Corp. (Harrison Division), Lockport, NY, August 21, 1991.

Mattingly, G.E., "Computed Gas Flow in Several Atomization Die Geometries," OIPM Atomization Consortium Meeting, NIST, Gaithersburg, MD, September 5, 1991.

Mattingly, G.E., "NIST Capabilities for Measuring Low Air Flowrate," Tylan-General, Torrance, CA, September 26, 1991.

Mattingly, G.E., "Optimal Parameterization of Flowmeter Performance," Tylan-General, Torrance, CA, September 26, 1991.

Presser, C., "The Structure of a Swirl-Stabilized Kerosene Spray Flame," 23rd Fall Technical Mtng., Eastern Section of the Combustion Institute, Orlando, FL, December 4, 1990.

Presser, C., "Determination of Droplet Characteristics in Spray Flames using Three Different Sizing Techniques," AIAA/ASME/SAE/ASEE 27th Joint Propulsion Conference and Exhibit, Sacramento, CA, June 25, 1991.

Presser, C., "Application of the Singular Value Decomposition to the Inverse Fraunhofer Diffraction Problem," ICLASS'91 - 5th International Conference on Liquid Atomization and Spray Systems, National Institute of Standards and Technology, Gaithersburg, MD, July 16, 1991.

Presser, C., "Effect of Dodecanol Content on the Combustion of Methanol Spray Flames," ICLASS'91 - 5th International Conference on Liquid Atomization and Spray Systems, National Institute of Standards and Technology, Gaithersburg, MD, July 16, 1991.

Rosasco, G.J., "Coherent Raman Spectroscopy of Collisional Line Shapes," Pittsburgh Conf. on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, March 6, 1991.

Rosasco, G.J., "Temperature and Pressure Information Derivable from Coherent Raman Spectroscopy," Applied Physics and Materials Science Seminar Series, Princeton University, Princeton, NJ, April 12, 1991.

Rosasco, G.J., "A Proposed Dynamic Pressure and Temperature Primary Standard," Workshop of the Measurement of Transient Pressure and Temperature, NIST, Gaithersburg, MD, April 24, 1991.

Rosasco, G.J., "High Resolution CARS Spectroscopy," Gordon Research Conference on the Physics and Chemistry of Laser Diagnostics of Combustion, Plymouth, NH, July 16, 1991.

Semancik, S., "Surface and Interface Properties of In Situ - Modified $Sn0_2(110)$: Spectroscopic and Electrical Studies," 37th National Symposium of the American Vacuum Society, Ontario, Canada, October 11, 1990.

Semancik, S., "Metal/Semiconductor Interfaces on $Sn0_2(110)$: Surface Chemical and Electron Transport Effects," 37th National Symposium of the American Vacuum Society, Ontario, Canada, October 11, 1990.

Semancik, S., "The Growth of Thin, Epitaxial $Sn0_2$ for Gas Sensing Applications," International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 26, 1991.

Semancik, S., "Epitaxial Oxide Films and Metal/Oxide Interfaces for Advanced Solid State Chemical Sensors, Gordon Research Conference on Inorganic Interfaces and Thin Films, Plymouth State College, Plymouth, NH, July 9, 1991.

Tarlov, M.J., "Temperature Dependence of the Interaction of Evaporated Silver with Self- Assembled Alkanethiol Monolayers on Gold," 179th Meeting of the Electrochemical Society, Washington, D.C., May 8, 1991.

Tarlov, M.J., "Interaction of Radio Frequency Oxygen Plasma with Self-Assembled Alkanethiol Monolayers on Gold," 13th Symposium on Applied Surface Analysis, American Vacuum Society, Minneapolis, MN, June 13, 1991.

Whetstone, J.R., "ISA Standard and Practices Board Procedures," ISA Washington Section Meeting, McLean, Va, November 6, 1990.

Zachariah, M.R., "Detailed Chemical Kinetic Modeling During Vapor Phase Condensation of Silicon/Silicon Dioxide: Comparison with Laser Spectroscopy Measurements," AIChE 1990 Annual Meeting, Chicago, IL, November 13, 1990.

Zachariah, M.R., "Oxidation and Pyrolysis of Silane During Particle Formation," 23rd Fall Technical Mtng., Eastern Section of the Combustion Institute, Orlando, FL, December 5, 1990.

Zachariah, M.R., "Formation of High T_c Superconductors in a Flame," 23rd Fall Technical Mtng., Eastern Section of the Combustion Institute, Orlando, FL, December 5, 1990.

Zachariah, M.R., "Chemistry of Silane Oxidation and Pyrolysis during Particle Formation: Comparison with In-Situ Measurements," Western States Section 1991 Spring Meeting, The Combustion Institute, Boulder, CO, March 18, 1991.

Zachariah, M.R., "Flame Synthesis of High T_c Superconductors," Western States Section 1991 Spring Meeting, The Combustion Institute, Boulder, CO, March 18, 1991.

Zachariah, M.R., "Aerosol Dynamics and Chemical Kinetics in Materials Processing: Examples from the Silicon-Oxygen System," Univ. of Arizona, Tuscon, AZ, May 23, 1991.

Zurlo, J.R., "Time-Based Polarization Ratio Measurements of Droplet Size," ICLASS'91 - 5th International Conference on Liquid Atomization and Spray Systems, National Institute of Standards and Technology, Gaithersburg, MD, July 16, 1991.

3. Patent Awards and Applications

Benson, K., A Differential Buoyant Force Densitometer (Submitted)

Kreider, K., Corrosion Resistant Thin Film Thermocouple (Submitted)

Kreider, K., High Seebeck Coefficient Thin Film Thermocouple (Submitted)

Semancik, S. and Cavicchi, R., Ultrathin, Highly-Ordered Tin Oxide Film Fabrication on Insulating Substrates (Submitted)

4. Committee Assignments

G.W. Burns
ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.04, Thermocouples
ASTM Subcommittee E-20.94, Publications
Instrument Society of American (ISA) SP-1.1, Committee on Temperature Measurement (Thermocouples)
The 7th International Symposium on Temperature: Its Measurement and Control in Science and Industry, Program Committee

P.H. Huang
ASHRAE SPC 41.6-82R Committee on Standard Methods for Measurement of Moist Air Properties

R.S. Kaeser
Philosophical Society of Washington (Treasurer)

K.G. Kreider
ASTM E20 Committee on Temperature Measurement
ASTM E20.04 Subcommittee on Thermocouples
IEEE Technical Committee on Sensor Standards, TC-9

A. Maček
AIChE Contacting and Separation Operations and Processes Group, Area 3b. Fluidization and Fluid Particle Systems
Combustion Institute - 24th Symposium (International) on Combustion, Program Subcommittee

B.W. Mangum
ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.03, Resistance Thermometers
ASTM Subcommittee E-20.06, New Thermometers and Techniques (Chairman)

ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.08, Medical Thermometry
  Working Group WG.02, Fever Thermometers
  Working Group WG.02A, Electronic Fever Thermometers
  Working Group WG.02B, Mercury-In-Glass Fever Thermometers
  Working Group WG.02C, Disposable Fever Thermometers
  Working Group WG.03, Continuous Clinical Temperature Monitoring Systems
  Working Group WG.04, Clinical Laboratory Temperature Measurement
ASTM Subcommittee E-20.90, Executive Subcommittee
Comité Consultatif de Thermométrie (of the CIPM) (Delegate)
National Conference of Standards Laboratories, Ad Hoc Committee 91.3 on The Change of the Temperature Scale (Chairman)
National Committee for Clinical Laboratory Standards (NCCLS), Temperature Subcommittee of Area Committee on Instrumentation, International Organization of Legal Metrology (OIML) Temperature and Calorific Energy Committee, RS4, Subcommittee on Electrical Thermistor Thermometers
The 7th International Symposium on Temperature: Its Measurement and Control in Science and Industry, Program Committee

G.E. Mattingly

ASME Main Committee on the Measurement of Fluid Flow in Closed Conduits
ASME SC-2 Subcommittee on Pressure Differential Devices
ASME SC-6 Subcommittee on Glossary of Terms for Flow Measurements
ASME SC-14 Subcommittee on Measurement of Fluid Flow Using Gravimetric and Volumetric Techniques (Chairman)
ASME SC-15 Subcommittee on Installation Effects on Flowmeters
ASME SC-16 Subcommittee on Vortex Shedding Type Flowmeters
ASME Main Research Committee on Fluid Meters
ASME SC-11 Subcommittee on Test Methods and Calculation Procedures (Chairman)
International District Heating Association: Testing Heat Meters Used in Fluid HVAC Systems
International Measurement Congress (IMEKO) Technical Committee No. 9 - Flow Measurement
Technical Advisory Committee for the GRI Sponsored Flow Metering Research Program at Southwest Research Institute

N.E. Mease

ASTM D22 Committee on Methods of Sampling and Analysis of Atmospheres
ASTM D22.02 Subcommittee on Methods of Sampling and Analysis
ASTM D22.05 Subcommittee on Calibration
ASTM D22.11 Subcommittee on Meteorological Measurement

E.R. Pfeiffer

ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.03, Resistance Thermometers

ASTM Subcommittee E-20.06, New Thermometers and Techniques
ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.08, Medical Thermometry

C. Presser
AIAA - National Propellants and Combustion Technical Committee Information Transfer Subcommittee (Chairman)
ASME K-6 Committee on Heat Transfer in Energy Systems
Combustion Institute - 24th Symposium (International) on Combustion, Publication Subcommittee

M.L. Reilly
ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.02, Radiation Thermometry Working Group E-20.02.01, Test Methods (Chairman)
ASTM Subcommittee E-20.06, New Thermometers and Techniques
ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.91, Editorial and Nomenclature

G.J. Rosasco
Combustion Institute - 24th Symposium (International) on Combustion, Program Subcommittee
7th International Symposium on Temperature - Its Measurement and Control in Science and Industry, Program Committee

J.F. Schooley
American Physical Society Topical Group on Instrument and Measurement Science (Chairman)
Philosophical Society of Washington (President)
7th International Symposium on Temperature - Its Measurement and Control in Science and Industry, Program Committee (Chairman)

M.G. Scroger
ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.04, Thermocouples
ASTM Subcommittee E-20.06, New Thermometers and Techniques (Secretary)

H.G. Semerjian
Combustion Institute - 24th Symposium (International) on Combustion, Program Subcommittee
ASME K-11 Committee on Heat Transfer in Fires and Combustion Systems
AIChE Engineering Sciences and Fundamentals Group, Area lb. - Kinetics, Catalysis and Reaction Engineering
AIChE Food, Pharmaceutical and Bioengineering Division, Area 15C - Biotechnology
ASTM E29.04 Subcommittee on Characterization of Liquid Particles

International Conference on Liquid Atomization and Spray Systems (ICLASS-91) July 1991 (Conference Chairman)
ECOWORLD'92, June 1992, Advisory Board

J.R. Whetstone
ISA Standards and Practices, Board of Directors

J.A. Wise
ASTM E-20 Committee on Temperature Measurement (Chairman 1988-1991)
ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers (Secretary)
ASTM Subcommittee E-20.08, Medical Thermometry
ASTM Subcommittee E-20.90, Executive Subcommittee (Chairman 1988-1991)
ASTM Subcommittee E-20.91, Editorial and Nomenclature (Secretary)

M.R. Zachariah
Combustion Institute - 24th Symposium (International) on Combustion Program Subcommittee

5. Other

a. Editorships

G.E. Mattingly
International Journal of Flow Measurement and Instrumentation (North American Editor)

H.G. Semerjian
Combustion Science and Technology, Special Issue (Co-editor)
Heat and Mass Transfer in Fire and Combustion Systems (Co-editor), ASME HTD-148 (1990)
Proc. 5th International Conference on Liquid Atomization and Spray Systems (ICLASS-91), NIST Special Publication 813, 1991 (Editor)

b. Seminars

November 7, 1990
Dr. Curtis Zimmerman, Clarkson University, Pottsdam, New York, "Preparation, Characterization and Modification of Fine Particles."

November 19, 1990
Professor James Gentry, University of Maryland, College Park, Maryland, "Diffusion Measurements of Spherical and Non-Spherical Aerosols."

January 3, 1991

Dr. Joseph T. Hodges, Institut Francais du Petrole, Paris, France, "Planar Laser Diagnostics in Fuel Jets via MIE Scattering and Exciplex Fluorescence."

January 23, 1991

Professor Erik Thiele, Northwestern University, Evanston, Illinois, "Deposition of Yttria-Stabilized Zirconia Thin Films Using Reactive D.C. Magnetron Sputtering."

February 13, 1991

Dr. Estela Blaisten-Barojas, John Hopkins University, Baltimore, Maryland, "Molecular Dynamics Study of Silicon Cluster-Cluster Collisions."

March 26, 1991

Dr. Gregory E. Poirier, University of Texas, Austin, Texas, "Scanning Tunneling Microscope Study of the Thermally Faceted TiO_2(001) Rutile Surface."

May 1, 1991

Dr. Nancy L. Garland, Naval Research Laboratory, Washington, DC, "Temperature Dependence of the Kinetics of the BO Radical."

May 2, 1991

Professor Jeanne M. Davidsen, University of Washington, Seattle, Washington, "The Coadsorption of Cyclic Hydrocarbons and Cesium on the Pt(111) Surface: Ensemble and Electronic Effects."

May 10, 1991

Dr. Bernard Tribollet, Universite Pierre et Marie Curie, Paris, France, "Small Electrodes for Wall Turbulence Study."

May 14, 1991

Cheryl K. Rofer, Los Alamos National Laboratory, Los Alamos, New Mexico, "Supercritical Water Oxidation Reactions for Waste Disposal."

June 7, 1991

Dr. Patrick Hebrard and Dr. Pierre Gajan, Office National d'Etude et de Recherches Aerospatiales (ONERA), Centre d'Etude et de Recherches de Toulouse (CERT), Toulouse, France, "Experimental and Computational Studies of Fluid Flows in Orifice and Vortex Shedding Flowmeters."

June 12, 1991

Dr. Michael S. Brown, Sandia National Laboratories, Livermore, CA, "High-Resolution Degenerate Four-Wave Mixing Spectral Profiles at Low Pump-Beam Intensity."

June 26, 1991

Professor M. Raja Rao, Indian Institute of Technology, Bombay, India, "Heat and Mass Transfer in Turbulent Bed Contactors."

August 21, 1991

James Vetrone, Northwestern University, Evanston, IL, "Fabrication and Properties of SnO_2 Epitaxial Crystal and Polycrystalline Films Grown by OMCVD."

c. Conferences/Workshops Sponsored/Co-Sponsored

October 22-26, 1990

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD

November 11-16, 1990

Combustion Reaction Engineering Session, American Institute of Chemical Engineers (AIChE) 1990 Annual Meeting, Chicago, IL

November 11-16, 1990

Novel Fluidization and Fluid Particle Systems Session, American Institute of Chemical Engineers (AIChE) 1990 Annual Meeting, Chicago, IL

November 13, 1990

ASTM E-20.06 Colloquium, San Antonio, TX

November 25-30, 1990

The Winter Annual Meeting of the American Society of Mechanical Engineers (ASME), Symposium on Heat and Mass Transfer in Fires and Combustion Systems, Dallas, TX

December 5, 1990

Intelligent Processing of Materials, Consortium Meeting, National Institute of Standards and Technology, Gaithersburg, MD.

December 5, 1990

Flowmeter Installation Effects, Consortium Meeting, National Institute of Standards and Technology, Gaithersburg, MD

January 14-16, 1991

East Coast Symposium on The Chemistry and Physics of Clusters and Cluster Ions, The Johns Hopkins University, Baltimore, MD

March 18-22, 1991

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD (Chair: B.W. Mangum)

April 23-24, 1991

Workshop on the Measurement of Transient Pressure and Temperature, National Institute of Standards and Technology, Gaithersburg, MD (Chairs: V.E. Bean and G.J. Rosasco)

April 26, 1991

International Conference on Metallurgical Coatings and Thin Films (ICMCTF'91), Thin Film Sensors and Microstructures Sessions, San Diego, CA (Chair: S. Semancik)

May 5-6, 1991

Instrument Society of America, Flow Short Course, San Diego, CA (Instructor: G.E. Mattingly)

May 7, 1991

ASTM E-20.06 Colloquium, Atlantic City, NJ (Organizer: B.W. Mangum)

July 15-18, 1991

Fifth International Conference on Liquid Atomization and Spray Systems (ICLASS'91), National Institute of Standards and Technology, Gaithersburg, MD

October 7-11, 1991

Synthesis of Powders by Spray Pyrolyses, Annual Meeting of the American Association for Aerosol Research, Traverse City, MI

October 21-25, 1991

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD

November 5, 1991

ASTM E-20.06 Colloquium on Infrared Thermometers for Medical Applications, San Diego, CA

November 19, 1991

High Temperature Processing of Materials Symposium, American Institute of Chemical Engineers (AIChE) 1991 Annual Meeting, Los Angeles, CA

November 21, 1991

Combustion Reaction Engineering Symposium, American Institute of Chemical Engineers (AIChE) 1991 Annual Meeting, Los Angeles, CA

December 2-6, 1991

CVD of Refractory Metals and Ceramics: In Situ Diagnostics, Materials Research Society, Fall Meeting, Boston, MA

December 1991

Spray Systems, 1991 ASME Winter Annual Meeting, Atlanta, GA

April 1992

Workshop on Transient Temperature Measurement, Seventh Symposium on Temperature, Its Measurement and Control in Science and Industry, Toronto, Ontario, Canada

SURFACE AND
MICROANALYSIS SCIENCE

VII. Surface and Microanalysis Science Division (837)

Rance A. Velapoldi, Chief

A. Division Overview

The Surface and Microanalysis Science Division (SMSD) was formed from the Surface Science Division and parts of the Gas and Particulate Science Division during the recent reorganization. This move brought together staff who are scientifically accomplished and productive. The new Division provides the capability of developing theories and performing research to characterize matter from the first monolayer of atoms or molecules to the microstructure of bulk material and to determine the processes that occur on surfaces and a microscopic scale, processes that are critical to the technological and natural worlds.

The Surface and Microanalysis Science Division conducts research and development to (a) determine the chemistry and physics of surfaces, interfaces, particles, and materials, and their interactions with a broad spectrum of species including electrons, photons, ions, atoms, and molecules; (b) determine the chemical and isotopic composition and electronic structure of surfaces, particles, and materials at nanometer scales and above; (c) determine the energetics, kinetics, mechanisms, and effects of processes occurring on solid and liquid surfaces as well as within materials (or devices); (d) use chemometrics to study the total chemical measurement process as well as source apportionment in atmospheric chemistry, and (e) develop and certify Standard Reference Materials and Standard Reference Data.

With the formation of the new Chemical Science and Technology Laboratory (CSTL), it was incumbent on the Laboratory to undergo major planning efforts during this formation year. In the process, six basic areas were identified as critical national areas of concern and developed as major components of the CSTL long range plan. One of those areas was **Surface, Interface, and Microstructure Characterization**, for which staff of this Division chaired the effort and had major input into the formulation of the long range plan. Thus a great deal of thought was put into the definitions, current research and future trends, application areas, and research opportunities and priorities for this Division. To facilitate exciting research ideas and areas, as well as to consolidate and strengthen the Division, it is necessary to acquire new funding; to this end, we have participated in more than eight initiative proposals, including the Atomic Scale Structure and Dynamics initiative in cooperation with the Physics Laboratory, and developed more than 20 Director's reserve proposals. Although we have received no new funding to date from the initiative efforts, decisions on the Director's reserve proposals are pending.

We were successful in obtaining funding for a new competence in Magnetic Engineering, and received partial funding for our efforts in Chemometrics from the Chemical Measurements Initiative proposed several years ago.

In spite of the upheavals associated with the reorganization and the prospect of a very tight budget climate for the Division in FY92, the staff continues to prove the merit of its research and development efforts by receiving recognition. **Richard Cavanagh**, working in close collaboration with staff from the Physics Laboratory, received the NIST Samuel Wesley Stratton Award, the oldest established NIST award "...for outstanding scientific or engineering achievements.." in laser studies of chemical dynamics. This work has resulted in numerous publications which have received outstanding peer reviews. **Dale Newbury** received the NIST Edward Uhler Condon Award for ".. distinguished achievement in effective written exposition in science and technology" for his publication "Microanalysis to Nanoanalysis: Measuring Composition at High Spatial Resolution". This invited contribution to the first issue of the journal Nanotechnology reviews, with pertinent examples, the measurement techniques and methods available for chemical analysis from micrometer to nanometer spatial scales. **David Bright** received the third highest Department of Commerce Award, the Bronze Medal, for "...his outstanding accomplishments in computer-aided imaging and analysis", of great import and utility in data manipulation and visualization in many areas including chemical compositional mapping at high spatial resolutions. **Robert Myklebust and Dale Newbury**, in collaboration with Sandia scientists, received the L. S. Birks Award of the Microbeam Analysis Society for "... the best contributed paper" presented at their international meeting in 1990. The paper, entitled "Applications of Parallel Computing to the Monte Carlo Simulation of Electron Scattering in Solids", describes real-time deconvolution of the chemical compositional spatial distributions for elements measured by electron probe instruments.

The breakdown of funding for Division activities during FY91 was as follows: NIST research funds (STRS) - 51.5%; Other Agency, non-Federal contract, and service analysis - 45.4%; and SRMP working capital funds for SRM certification - 3.1%. However, it must be recognized that the formation of the Surface and Microanalysis Science Division joined together groups that are quite different from a funding perspective, a factor which definitely affects the focus of the individual groups. For example, NIST STRS for each group ranged from 29 to 96%. Despite differences in funding sources, all four groups provide world-class expertise and are exceptionally productive with more than 140 publications and reports and more than 125 regional, national, and international talks (approximately 50% invited). These efforts, when combined with staff efforts on various committees and working groups, for example, ASTM, AVS, IUPAC, ISO, MAS, IAEA, ANSI, VAMAS, and IUVSTA, the organizing of international and national conferences, the evaluation and consulting panels for DoE, DoD, USGS, NSF, EPA, NRC, USGS, WHOI, and industrial groups, all demonstrate strong interactions by the staff with our constituents and effective technology transfer.

The following comments are a general overview of some staff's efforts by Group; specific information on their individual contributions can be found in the **Technical Activities Section** for this Division. The overview and the specific activities exemplify our interactions which have impacts on specific technical areas.

The **Atmospheric Chemistry Group** continues to make fundamental contributions to the areas of atmospheric measurements and standards and chemometrics. They provide leading-edge research in micro-accelerator mass spectrometry target preparation and chemistry. For example, their efforts in applying factorial design and on-line mass spectrometry to optimize microgram carbon target chemistry have resulted in significant advances to existing methodology. The applications of their advances are critical in extensive local, regional, and global studies of source apportionment (anthropogenic and natural) for volatile organic compounds, methane, carbon dioxide, carbon monoxide, and natural gas. A substantial contribution has been made to the new, high priority international (IUPAC) environmental initiative in the form of an exhaustive review of atmospheric particle source apportionment. The NIST Primary Standard Reference Ozone Photometer, for which the software and hardware are being updated, continues to be the benchmark standard for the national (EPA-ten instruments) and global (Canada, Sweden) network on which worldwide ozone measurements are standardized.

Increased efforts in the Chemometrics program have been possible through a small infusion of funds from the Chemical Measurements Initiative. Strong planning efforts at the beginning of the year resulted in selected activities that are already underway, including: pre-liquid chromatographic organic species separations (with Division 835); DNA fingerprinting (with Div. 831 and the FBI); automated particle analysis (with the Microanalysis Research Group); standard test data for algorithmic quality control; and a possible project on the chemical fingerprinting of pharmaceuticals (with FDA). Important fundamental work has been done on multivariate data structure, quality, fundamental analytical limits (detection, quantification, identification), and accuracy -- closely integrated with and guided by the needs of national and international organizations. Such work has become critical for common understanding, quality communications, and technology transfer in analytical science.

The **Microanalysis Research Group** continues its leadership in measurements, standards development, and applications for microprobe analyses. The Group is deeply committed to and supported by other government agencies, and to the NVLAP laboratory accreditation program, which has approximately 950 laboratories enrolled. Three specific accomplishments underscore the breadth of their efforts. First, in the continuing effort to push measurement capabilities to higher spatial resolution and lower concentrations, a major breakthrough has been achieved in trace nanoanalysis. Using the NIST-NIH Nanometer Analysis Facility, 50-200 ppm levels of trace transition and rare-earth elements in a thin glass have been measured in a volume with dimensions of 10 nm x 10 nm x 100 nm. This volume contains a total of approximately 1×10^6 matrix atoms of silicon, sodium, aluminum, calcium, and oxygen; thus signals from 50 to 200 atoms are being observed. Second, Desktop Spectrum Analyzer (DTSA), software that provides mathematical algorithms based on first principles for complete generation, analysis, and correction of electron beam excited x-ray spectra (EPMA, AEM, SEM) has been finished (patent applied for) and is for sale by the Standard Reference Data Program. The program will be extended to other spectroscopies in the future. Third, two asbestos SRMs to aid in the asbestos laboratory accreditation program have been finished and transferred to the SRMP: SRM 1866a Bulk Asbestos-Common [Chrysotile, Grunerite (Amosite), Riebeckite (Crocidolite)]; and SRM 1876b Chrysotile Asbestos for Quantitative Transmission Electron Microscopy. These three accomplishments, combined with the other efforts in particle analysis, and quantitative elemental and molecular compositional mapping with probe instruments, define the Groups commitment to research, applications, and technology transfer.

The **Surface and Dynamical Processes Group** utilizes novel, state-of-the-art measurement techniques along with conventional surface sensitive probes to elucidate the underlying mechanisms for surface reaction processes. Present efforts are focused on the characterization of laser-induced processes and the utilization of electronic spectroscopies to characterize the chemistry of multicomponent film growth. Two highlights from each focus area follow. First, novel state-resolved diagnostics of molecular desorption, initially developed at NIST for the study of reactions on metal surfaces, have been applied to laser-induced desorption from semiconductors. The research established that surface-localized electronic excitations, previously neglected in analysis of photochemistry, can directly induce reactions. These studies are now being extended to laser-induced photolysis of metal deposition precursors. Second, femtosecond time-resolved probes have been used for the first time to follow the energy transfer and relaxation of vibrationally excited adlayers on metal surfaces. This world-class effort has resulted in the first determination of the temporal evolution of the spectrum of an adlayer of highly excited adsorbates. The results are in qualitative accord with simple theories and have already stimulated more detailed theoretical and experimental efforts.

Third, an ultra-high vacuum, thin-film production and measurement system has been designed and fabricated to understand and control the surface processes and parameters that affect the growth and modification of surfaces and thin films. The system provides the flexibility to vary, for example, the growth conditions of thin-film materials so that the different materials formed can be investigated and their physics and chemistry understood. The first studies include programmed growth of high T_c films with computer control of the 3 metal (Dy, Ba, Cu) evaporation sources and the capability to examine various deposition parameters using surface science probes (RHEED, LEED, etc.). Additionally, *in situ* oxidation via O_3 provides for film growth at reduced temperatures. Last, the ellipsoidal mirror analyzer experimental station, designed and built at SURF-II, is operational and can be used to correlate electronic properties with chemical properties for a broad range of materials including oxides, ferroelectrics, metals, and superconductors. Compared to conventional techniques, the time necessary to obtain data (images) has been reduced by several orders of magnitude by simultaneously measuring the energy and momentum of photo-emitted electrons. Initial measurements have been made to determine the Fermi surface as well as functions possibly related to the electron densities between atoms for clean Ru(0001) and for adsorbed oxygen on its surface.

The Thin Films and Spectroscopies Group has had a productive year with significant accomplishments in its three main areas of activity. First, a substantial expansion in magnetic engineering was accomplished as a result of Director's Reserve funding in FY91 and new competence support in FY92. A major upgrade has been made in the experimental facilities in our ability to fabricate thin-film structures, to characterize them structurally and chemically by several complementary techniques, and to determine their magnetic properties - all *in situ*. In experiments conducted with the previous equipment, an unexpected factor-of-two enhancement was found in the magneto-optical polar Kerr rotation of Fe/Cu/Fe thin-film structures for Cu thicknesses of about 7 monolayers over that expected from bulk iron. This work demonstrates the sensitivity of magnetic properties to structural properties and shows the potential of enhanced Kerr rotation in thin-film structures for improved magneto-optical recording.

The second main area of activity involves the provision of needed reference data for the surface analysis techniques in common use [Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and sputter-depth profiling (SDP)] and the development of improved methods so that more reliable and accurate compositional measurements can be made. Major progress has been made in a series of calculations of electron inelastic mean free paths (presently a major limitation in quantitative surface analyses by AES and XPS) for a group of 42 materials and, from an analysis of the trends, the development of a predictive formula for other materials. In other work, certification of the new chromium/chromium oxide marker layer thin-film depth-profile standard (SRM 2136) has been completed and the material is now on sale. An important component of the Group effort here is the strong involvement with national and international standards committees developing standards for surface analysis.

In the third area of work, new theories of surface measurements and spectroscopies are developed. New models have been devised for describing electron negative-ion resonance states that are important in inelastic tunneling through quantum-well nanostructures, stimulated desorption at surfaces, and laser-excited hot-electron dissociation and desorption processes. The insights obtained from this research have been formulated into a promising new view of electron femtochemistry at surfaces. In other work, new calculations have been made of electron transmission at interfaces of silicon with nickel and cobalt disilicides for comparisons with measurements made by ballistic electron emission microscopy; agreement with the limited amount of experimental data shows the importance of band structure in this method of probing interface properties.

It is a pleasure to report that a patent was awarded to Terrence Jach in April for his invention (with colleagues in the NIST Electronics and Electrical Engineering Laboratory) of a Diffraction Device Which Detects the Bragg Condition. This device, which combines the functions of x-ray diffraction and detection, is useful for stabilizing the monochromatic high-energy x-ray radiation produced in synchrotron light sources.

This brief overview, coupled with the research efforts described in the Selected Technical Reports Section, provide some idea of the general directions we have followed during the past year. In FY92, we hope to stabilize current funding, continue the planning process started with the development of the long range plan, reorient some existing funding, and obtain new funding for cross group and divisional projects.

B. Selected Technical Reports
(Surface and Microanalysis Science Division)

1. Sources of Fine Carbonaceous Aerosol in Urban Atmospheres Using Carbon Isotope Analysis

D.B. Klinedinst, G.A. Klouda, L.A. Currie, L. Hildemann (Guest Scientist), and G. Cass (Guest Scientist)

A suite of 16 fine aerosol samples, each sample representing a unique source, was collected in the Los Angeles Basin using a specially designed dilution sampling system. The sources chosen represented approximately 80% of the fine primary organic aerosol emissions to the Los Angeles air-shed, based on previous engineering estimates. A chemical characterization of these samples revealed that more than 40% of organic aerosol emissions were from anthropogenic pollution sources that emit contemporary (non-fossil) aerosol carbon. This conclusion was in good agreement with previously published radiocarbon (^{14}C) data of ambient fine carbonaceous aerosol in the Los Angeles area. Since these source samples were unique in terms of both scope and quality, archived aliquots of these same samples were taken for an accurate determination of contemporary carbon by direct measurement of the radiocarbon (^{14}C) abundance via Accelerator Mass Spectrometry (AMS).

Following the sample preparation techniques developed at NIST for microgram size samples, total carbon fractions were separated from all samples and elemental carbon fractions were isolated from a subset of 10 source samples. Total carbon was (1) converted to CO_2 in a quartz furnace at 950 °C in the presence of O_2, (2) passed over hot Pt/CuO to ensure complete conversion, and (3) trapped at 196 °C; the entire process was accomplished in a vacuum manifold under dynamic conditions. A separate aliquot was treated with nitric acid to remove organic carbon, then the residue (elemental carbon) was oxidized to CO_2 as stated above. At the moment, samples await conversion of CO_2 to Fe-C (bead) targets suitable for ^{14}C AMS measurements. This conversion is accomplished by reducing the CO_2 to CO over hot Zn followed by the reduction of CO to graphitic carbon on hot Fe wool catalyst in the presence of H_2.

The ^{14}C data for these source samples, in conjunction with a mathematical transport model, will be used to calculate the fossil and contemporary (particulate) carbon concentration expected for a one-year period at two different sites in the Los Angeles area. Prediction validity will be evaluated by comparison to AMS ^{14}C results of 4 ambient samples, each representing a 3-month composite, collected in Long Beach and Azusa.

2. Factorial Design Techniques Applied to Optimization of AMS Graphite Target Preparation

R.M. Verkouteren and G.A. Klouda

A large number of factors influence the preparation and quality of graphite targets for ^{14}C accelerator mass spectrometry (AMS). We identified four factors (sample size, catalyst temperature, H_2 pressure and pretreatment time) as potentially critical, and investigated their effects on two particular characteristics: the integrated rates of CO_2 reduction (to graphite) and methane production.

We used a 2-level, fractional, factorial experimental design, where sample size was 50 or 500 µg C, catalyst temperature was 450 or 600 °C, hydrogen pressure was 0 or 30% of total pressure, and pretreatment time of the catalyst (heated at 300 °C in 1 bar H_2) was 0 or 4 hours. Chemical reduction yield rates were calculated from measurements using absolute manometry and mass spectrometry.

Chemical reduction yield rates ranged from 0.2% to 6.2% per hour. With respect to their influence on percent yield rate, the major factors we studied were ordered as: sample size > level of hydrogen > pretreatment of the catalyst. The temperature of the catalyst, and a cross factor for sample size and hydrogen pressure, were only marginally influential. Other interactions did not appear to be significantly important. We estimated uncertainty in the order of influence and magnitudes of the effects by a bootstrap procedure based on the Monte Carlo method.

Significant methane production was observed in only one experiment, suggesting that methane originates from indigenous carbon in untreated iron catalyst only in the presence of hydrogen and only at 450 °C. We expected H_2 levels to remain steady during the reductions; surprisingly, H_2 pressures increased during all but one experiment. We attributed this phenomenon to reduction (by zinc at 450 °C) of desorbing H_2O vapor.

These results showed that to optimize reaction rate and yield, reductions should be performed on pretreated iron catalyst in the presence of hydrogen (30% of total pressure). Small sample sized will require extended reduction times. The temperature of the catalyst should be set at 600 °C to avoid possible CH_4 production. This investigation indicates that factorial design techniques are a useful means to investigate multivariate effects on the preparation and quality of AMS graphite targets.

3. DNA Fingerprinting: Error Structure and Analysis

D. Duewer, L.A. Currie, D.J. Reeder (831), S.D. Leigh (CAML), H.K. Liu (CAML) J.J. Filliben (CAML), R. Paule (CAML), and J. Mudd (Guest Scientist)

The FBI Academy has developed a prototype system for matching DNA-containing tissue to suspect individuals, using commercial restriction fragment length polymorphism (RFLP) analysis. As of October 1, 1991, they had completed three rounds of interlaboratory comparison studies in an effort to characterize this prototype system. The comparison studies had been designed to explore the impacts of: band sizing alone, chromatography confounded with band sizing, and sample preparation confounded with both the chromatography and the band sizing. NIST has been a participating laboratory in all rounds of the comparison studies. Shortly after the completion of the third round, the FBI requested NIST assistance in the interpretation of the accumulated data. They were particularly interested in obtaining NIST validation of their assumptions regarding the impact of measurement error on the utility of a multi-laboratory national database of RFLP data on convicted sex offenders. An initial meeting, involving the FBI representatives and NIST chemists and statisticians, was held in August.

Following the August meeting, the FBI supplied all data from the completed interlaboratory studies and initiated a fourth round to permit characterization of the system over the complete range of accessible fragment lengths. The supplied data were first reformatted into a more easily analyzed format and distributed to all involved NIST data analysts. The data proved insufficient for formal interlaboratory comparison analysis. Initial chemometric analysis focused on characterization of the variance of replicated individual RFLP bands as a function of their mean value. Two variance components were identified: a small constant variance associated with the chromatography and an approximately proportional standard deviation associated with the band sizing. An empirical equation fitting the variance to the mean band size was derived. The predicted standard deviation over the entire range of band sizes explored proved considerably smaller than the bin-widths used in the FBI's matching algorithms, suggesting that their assumptions are indeed sufficiently conservative.

4. Trace Nanoanalysis: Chemical Characterization with High Spatial Resolution and Near Single-Atom Sensitivity in Dilute Systems

D.E. Newbury

Microanalysis techniques based on beams of electrons, ions, and photons provide spatial selectivity over the dimensional range from micrometers to nanometers. Based on these dimensions, the analyzed sample mass ranges from picograms to attograms, which seems to suggest that microanalysis techniques have the inherent capability to achieve trace sensitivity. However, because of limitations imposed by the physics of signal generation and measurement, most microanalysis techniques are limited to detecting relatively modest minimum concentration levels, typically in the range from 100 to several thousand parts per million or even higher. The exception to this situation has been microbeam mass spectrometry (secondary ion mass spectrometry, laser microprobe mass spectrometry). For an analyzed mass in the picogram range, microbeam mass spectrometry can achieve detection limits of parts per million to parts per billion for many elements. When higher spatial resolutions are desired, and the analyzed mass decreases, even the microbeam mass spectrometry methods suffer from significantly reduced sensitivity.

Trace nanoanalysis, the detection of trace constituents from volumes with nanometer dimensions, has now been achieved by parallel detection electron energy loss spectrometry (PEELS) in the field emission scanning transmission electron microscope (FE-STEM), a form of analytical electron microscope, at the NIST-NIH Nanometer Analysis Facility. PEELS measures the characteristic energy losses associated with ionization of atomic shells suffered by energetic beam electrons that pass through a thin (100 nm or less) specimen. The electrons transmitted through the specimen are dispersed with a magnetic sector spectrometer. Parallel detection is achieved by electron-to-light conversion with a scintillator, which in turn is viewed by a high sensitivity charge-coupled device with 1024 discrete elements. Trace nanoanalysis has been successfully demonstrated by using particles of NIST SRM 610 (Trace Elements in Glass) as a test specimen. PEELS spectra were obtained in the direct and difference modes. The difference mode consists of taking a sequence ($-\Delta E$, 0, $+\Delta E$) of spectra with each spectrum slightly shifted in energy (e.g., $\Delta E = 6$ eV). The spectra are subtracted and scaled, which has the effect of eliminating the channel-to-channel gain variations that would otherwise overwhelm characteristic features from trace constituents. The second difference spectrum revealed the presence of more than 20 constituents in SRM 610, including transition and rare earth elements, present at levels ranging from 50 - 200 parts per million atomic. The beam was scanned over an area 10 nm x 10 nm, and the specimen thickness was estimated to be less than 100 nm so that the mass sampled by the beam contains approximately 1 million atoms of the glass matrix elements: oxygen, sodium, silicon, aluminum, and calcium. The detection of each trace constituent thus corresponds to the measurement of 50-200 atoms in the analyzed mass. The strength of the characteristic signals from these trace elements suggests that the ultimate detection limit is fewer than 10 atoms, and may actually extend to single atom sensitivity. Most importantly, this measurement suggests the possibility of trace detection in materials of practical importance where the analytes of interest are diluted to technologically important levels. A possible application is the study of the distribution of doping elements in semiconductors, particularly near interfaces where the spatial resolution of the AEM-PEELS technique will be of special benefit.

5. Fundamental Raman Measurements toward a Quality Assurance Measurement Standard for CVD Diamond

E.S. Etz and D.E. Newbury

The present technology of the chemical deposition of diamond and diamond-like coatings is leading to products and devices that are expected to have a major impact in numerous high-technology applications. Diamond possesses a broad array of properties which make it exceptional. These properties also make it an attractive material for a variety of industrial uses, among them machine tools, bearings, passive coatings, UV/IR optics, semiconductors, and heat sinks. This new diamond technology is beginning to play a major role in the commercialization of a range of products, in large part due to advanced methods of chemical vapor deposition (CVD) that produce synthetic diamond as bulk material, freestanding slab, hard coatings, and thin films. This industry has arrived at a juncture where quality control measures are an important part of manufacturing operations. Thus, the need has been expressed for calibration standards and standard measurement methods to be developed for characterizing the chemical and physical properties of CVD diamond.

To assess the quality of diamond, industry and other research laboratories are routinely applying Raman spectroscopy as the benchmark analytical technique for characterizing diamond and diamond-like carbon. Our work on CVD diamond has focused on the application of Raman microprobe spectroscopy for determining the quality of thin diamond films deposited on various substrate materials. The film properties are correlated with deposition conditions, i.e., the composition of the reactive gas (H_2/CH_4 mixture), temperature, rate of nucleation and growth, and film morphology. We have made Raman measurements to determine the purity of the diamond phase, to recognize graphitic and amorphous carbon impurities, to estimate strain effects and to examine laser-induced photoluminescence emissions from lattice defects and vacancies. The measurements have been performed on diamond deposits and polycrystalline thin films produced by both hot filament and microwave-assisted CVD methods. In general, the spectra of single diamond microparticles (size range 1-15 µm) formed in the early stages of nucleation show a high-purity diamond phase. As nucleation progresses and a continuous film is formed, a graphitic carbon component is often detected. A photoluminescence band at 1.68 eV observed in the Raman spectrum is indicative of a lattice vacancy. Microprobe measurements on cross sections of films have allowed us to examine the film-substrate interface. In these spatially resolved measurements we have shown the existence of a distribution of various compositions over parts of the film area attributed to spatially non-uniform conditions of the deposition process. Using these results, we have designed a measurement protocol to examine homogeneity of composition with micrometer spatial resolution, and to establish the criteria for good and bad CVD diamond based on the features of the Raman spectrum.

These studies have focused on defining the properties of a reference material thin diamond film to assess the quality of diamond. Thus, following discussions with industry and the research community, we have now proposed a standard for the chemical characterization of CVD diamond by Raman spectroscopy. This reference material will consist of a diamond film on silicon wafer, characterized on the basis of its Raman spectrum. Discussions are underway with several representative diamond industries to make this standard as broadly applicable as possible.

6. Analysis of Desert Southwest Aerosol Particles by Laser Microprobe Mass Spectrometry

S.M. Hoeft, R.A. Fletcher, and E. Machias (Guest Scientist)

In recent years, episodes of haze have been more frequent in the desert southwest, resulting in the degradation of scenic views in pristine areas. At issue is the composition of the aerosols responsible for the haze, since the composition is strong evidence of the particle's source. Studies of filter samples indicate sulfates, nitrates, crustal materials, and carbonaceous aerosols can contribute to the episodes of haze in this region.

Using microanalytical techniques on size-segregated aerosol samples, information is obtained that is usually not available from 'bulk' analysis. Typical 'bulk' studies involve the collection of particles with diameters less than 2.5 micrometer on a filter, and the average chemical composition is determined for all the particles. This composition is then used for source apportionment or visibility studies. Aerosols with physical diameters in the range 0.1 to 1.0 micrometers scatter light more efficiently than larger aerosols, thus visibility studies need more information on the composition of this size fraction of particles. The spatial resolution of the laser microprobe (LAMMA 500) allows analysis of single particles with diameters as small as 0.3 micrometers and in some cases even smaller. The instrument's time-of-flight mass spectrometer has high sensitivity and is capable of detecting several classes of compounds often found in ambient aerosols.

The major use of the LAMMA 500 has been for investigating the qualitative composition of aerosols collected from a remote sampling site. Washington University is participating in a long-term pollution transport study with the Desert Research Institute (Reno, Nevada), which operates the sampling site in southern Nevada. Ambient aerosol samples taken during haze episodes are being compared with those taken during periods of good visibility.

The results from analyzing single particles correlate with the 'bulk' results. However, one result from this study is that sulfate particles, which make up a large fraction of the aerosol population, have two distinct chemical forms with different size distributions. The two types of sulfates detected are sulfate rich in hydrogen and sulfate rich in sodium. The hydrogen type sulfate was found most often in small sized particles (0.1-0.5 micrometers) and the sodium type predominantly in larger particles (0.5-1.0 micrometers). More work is needed to determine if these two forms are independent, i.e., two different sources, or if they represent different products of the chemical reactions sulfates undergo in the atmosphere. Analysis of single particles can establish the heterogeneity of the particles, which is impossible to do by 'bulk' techniques. The simultaneous occurrence of sulfate and carbon can be seen in the spectra of individual particles with diameters of 0.5 micrometers and larger. In this size fraction, the sulfates were found without carbon, but carbon was rarely found without sulfate.

7. Quantitative 3-Dimensional Chemical Imaging Using Secondary Ion Mass Spectrometry

J.G. Gillen

With the size of state-of-the-art microelectronic circuits rapidly reaching sub-micrometer levels, characterization of electronic device structures becomes a formidable challenge requiring the development of analytical techniques capable of both lateral and in-depth elemental localization. We are currently developing the capability for 3 dimensional (3D) elemental compositional mapping of electronic devices using Secondary Ion Mass Spectrometry (SIMS). As one of the most widely used tools for semiconductor characterization, SIMS offers ppm-ppb detection limits, sensitivity to all elements in the periodic table, secondary ion imaging, and depth profiling. One of the most powerful, and so far under-utilized, capabilities of SIMS is 3D elemental depth profiling. In this approach, a series of secondary ion images for an element or elements of interest is acquired as a function of time; each image corresponds to the elemental lateral distribution at a given depth below the original sample surface. Using recently developed volumetric imaging techniques and NIST-developed software, this "stack" of images can be reconstructed into a 3D representation of the elemental composition in the near-surface region of an electronic device. These images have a typical lateral resolution of 0.2-1 micrometer and a resolution in depth that may approach 1 nm. While the qualitative localization of dopants and matrix species in electronic devices is extremely important, correct device operation also requires that these species be incorporated at the appropriate concentrations. Therefore, our work is aimed at developing the capability for quantitative 3D elemental imaging.

Initial studies have involved assembling the computer hardware and obtaining or writing the necessary software to process and quantify an image stack containing 50-100 images (3-10 Mbytes). In a typical analysis, a sequence of elemental images from a standard ion implant is acquired as a function of increasing depth into the sample. Each of these images is normalized to a uniformly distributed matrix ion species. Using a selected region in the center of each normalized ion image, (to avoid edge effects), the pixels are summed to generate a selected area depth profile. From the known dose of the implant, the integrated counts under the implant peak (after background subtraction), and the depth of analysis, a relative sensitivity factor (RSF) is calculated. This RSF can then be applied on a pixel-by-pixel basis to an image depth profile of the same element with an unknown concentration.

Using the ion microscope SIMS instrument, we have been able to quantify fully, in 3 dimensions, the elemental concentration distribution of a variety of dopant species in ion implant standards and simple electronic device test structures. We are presently exploring the capabilities of this technique for more practical "on chip" device analysis and for the characterization of metallic superlattice structures.

8. Profiling Deuterium Through Silicon Dioxide Films by Secondary Ion Mass Spectrometry

D.S. Simons and P.H. Chi

Hydrogen in SiO_2 has been extensively studied because of its implication in the degradation of electronic devices. It has been proposed that hydrogen reacts with silicon dangling bonds to form Si-H bonds, precursors for trap generation. Thus, there is a strong interest in determining the location of hydrogen in layered SiO_2/Si structures following various processing treatments. Secondary ion mass spectrometry (SIMS) can determine the hydrogen concentration as a function of depth. An instrumental hydrogen background signal is always found due to the presence of water vapor in the residual vacuum of the instrument. If deuterium is substituted for natural hydrogen as the gas to which samples are exposed during treatment, the instrumental background will be lower by a factor of 7000 compared with the major hydrogen isotope. Deuterium concentrations have been calibrated with relative sensitivity factors (RSFs) for D/Si determined from SIMS depth profiles of separate ion implants of deuterium in Si and in an SiO_2 film on Si. We found that the RSFs for deuterium in Si and in SiO_2 were identical within the experimental error of ±10%, when cesium primary ions were used for bombardment and positive secondary ions were detected.

As a practical application of deuterium profiling by SIMS, samples of SIMOX (separation by implanted oxygen) material were annealed in pure deuterium at either 850 °C or 1000 °C by scientists at the Naval Research Laboratory. SIMOX is created by implanting a silicon wafer with a high dose of oxygen to form a buried oxide layer. The material is normally annealed at a temperature in excess of 1300 °C to remove implantation-induced defects and to regrow high quality single crystal silicon above the buried oxide. By profiling blank SIMOX wafers that had not been annealed in deuterium, we determined that the detection limit for deuterium in the silicon phase was about 10^{18} atoms/cm^3, whereas the detection limit in the oxide was 10^{16} atoms/cm^3. In SIMOX material that had been annealed at high temperature prior to deuterium exposure, we found that the deuterium was at background levels in the top silicon film and in the silicon substrate. It was rather uniformly distributed in the buried oxide at a level of about 10^{19} atoms/cm^3 except at the Si/SiO_2 interfaces where the deuterium concentration was a factor of 10 higher. In contrast, for SIMOX that had not undergone a high temperature anneal, deuterium accumulated in the top silicon film to a level greater than 10^{20} atoms/cm^3, whereas the level in the oxide was similar to the other samples. The interpretation of the SIMS data is that, in annealed SIMOX, deuterium diffuses rapidly through the surface silicon film and attaches to silicon dangling bonds and oxygen vacancies in the buried oxide. In unannealed SIMOX, additional deuterium is trapped in the surface silicon by implantation-induced defects and residual implanted oxygen. These studies can be used in conjunction with electrical measurements to correlate performance degradation of devices made on SIMOX with hydrogen content and distribution.

9. Microarea Quantitative Chemical Analysis with Time-of-Flight Secondary Ion Mass Spectrometry

J.A. Bennett and D.S. Simons

The combination of time-of-flight mass spectrometry (TOF-MS) and liquid metal ion source (LMIS) technology has created the potential for an efficient and sensitive method of collecting secondary ions sputtered from microareas (less than 1 μm^2). However, information relevant to ion beam microanalysis (e.g., sample preparation, sample form, instrumental parameters, relative sensitivity factors [RSF], etc.) is somewhat limited. We have undertaken a systematic investigation of the factors that affect the quantitation of secondary ion mass spectrometry (SIMS) data obtained from reference glass samples with a Ga LMIS and TOF-MS.

Initial work has focused on factors that influence the precision and accuracy of RSFs determined for elements in a glass matrix. Reproducibilities on the order of ±15% can be obtained both within and among glasses of similar composition provided the sample surface is sputter-cleaned with a dose of at least 4×10^{16} ions/cm^2 prior to the collection of secondary ions. The reproducibility varies as a function of sample form. Irregularly shaped samples, i.e., glass shards and spheres, showed poorer precision than flat, uniform samples of the same composition. The accuracy of the RSFs was also a function of the sample form. Several elements in glass shards gave sensitivity factors that were about a factor of 2 higher than for the bulk form. In the bulk form, many reference glasses are electrically insulating and are subject to charging during bombardment with ions. A pulsed low energy electron beam can be used to compensate for the build-up of charge in the sample. If, however, the charge build-up is not entirely compensated, the secondary ion transmission efficiencies can be affected. If the change in transmission efficiency is not equal for all secondary ions, then the RSFs will change. As a result, in glasses where charge compensation was not required, the RSFs did not change as greatly from shards to bulk as when compensation was needed.

The detection limits obtainable with our system were determined from data on the useful yield of elements in a thin glass film. The useful yield is defined as the (ions of A detected)/(atoms of A sputtered). Values of 3.1×10^{-3} and 8.2×10^{-3} were determined for Mg and Ca, respectively. Using a range of useful yield values of 10^{-2} to 10^{-5} and confining the analysis area to the instrument's smallest primary beam diameter of 0.2 µm and a sampling depth of 10 nm, the predicted detection limits would range from 0.1% to 10% by weight. Detection limits will improve as the useful yields increase. The useful yields reported here for Mg and Ca show a factor of 10 increase over previously recorded values. The increase resulted from an improvement in secondary ion transmission optics. Another factor of 2 increase is expected following further modification of the optics.

10. LISPIX: Applications for Image Analysis and Microscope Automation

D.S. Bright

The Microanalysis Research Group uses electron microscopes coupled with VAX computers to acquire and analyze images. FORTRAN in the VAX/VMS environment handles the large image arrays and communicates with the electron microscopes. Part of the LISPIX system, written in FORTRAN, provides lower level functions such as: a) moving the stage of the electron microscope to given coordinates, b) collecting an image c) thresholding, blobbing or performing elementary arithmetic operations on images, d) scaling, filtering, enhancing and displaying images, and e) making concentration histogram images from groups of images. A user can control this part of the system by typing in the name of the command with various parameters. For larger tasks, such as an image collection run or a particle size analysis, many commands must be given in sequence. This requires extensive typing, more elaborate functions, or a higher level of control. VAX FORTRAN is a compiled language which presents an inconveniently long edit-compile-link-run cycle. This is not a problem for writing the lower level functions, which are used often but rarely need modification. On the other hand, the functions that do the higher level tasks may require frequent modification to meet research needs. Occasionally, extended functions are implemented in FORTRAN, but most of the day-to-day work is done using LISP functions for a higher level of control.

VAX COMMON LISP was first used to advantage for this because of the fast edit-compile-link-run cycle, the flexible data structures, and the natural advantage of the language for writing many related functions. However, running LISP and FORTRAN together on one VAX slowed the lower level functions, compared with running the FORTRAN part of the system alone. This decrease in computing efficiency by a factor of three to ten inhibited efficient use of the microscopes. MacIntosh Common LISP is able to run all of the algorithms developed on the DEC LISP, with very little change, and offers a good programming environment and well developed tools for making a user interface. Third party software was adapted to connect the MacIntosh, running LISP, over an existing Ethernet to the VAX. The group already had several MacIntoshes and VAX'es, all already networked, so that the LISPIX system can run on whatever computers are available with no additional wiring. Running LISP on the MacIntosh has enhanced the LISPIX system in several ways: a) The system runs much faster. The lower level functions run just as fast as when used directly by an operator typing commands to the VAX. b) The well developed user interface of the MAC has been incorporated to provide menus for instrument control and image display functions and obviate the need to remember special command sequences. c) Graphics and point-and-click functions allow quick selection of image frames or particles within an image. Coupled use of two computers for our image acquisition and analysis allows us to take advantage of the existing VAX-microscope combinations and of the user interface tools on the MAC. The LISPIX system runs faster when the VAX is not burdened with LISP. Dividing the computation task into two smaller parts simplifies debugging, especially since communication between the two computers consists of human readable messages -- precisely what an operator would type or read when using the FORTRAN part alone. And, the FORTRAN part is useful as a stand alone system for simple tasks or instrument setup.

11. Automated Electron Microscopy

J.A. Small and M. Calderone

Automated particle analysis (APA) is used to provide elemental and morphological information on particulate populations. In this procedure, the electron beam and specimen stage are computer controlled, and a series of particles, usually numbering from a few hundred to a few thousand, are analyzed. Based on morphology and composition, the different particles are divided into groups. The groupings can be either preselected categories (discriminant analysis), or categories selected on the basis of the analytical results (cluster analysis). The different particle groupings that are determined can then be used to characterize the particulate population. This type of analysis is often used in environmental studies to identify various sources that contribute to a sampled aerosol.

To date there have been no detailed APA studies of controlled, (i.e., standard) particle populations for the purpose of assessing the limitations associated with APA and the post-collection data reduction. One of the major limitations in APA is a lack of information on the accuracy and precision of the elemental analyses. In APA, x-ray collection times are often short (less than 20 s), which limits the counting statistics. In addition, the accuracy of elemental results from particles may be severely compromised by the particle morphology. These limitations may have a dramatic effect on the ability of the data-reduction methods to distinguish between similar but unique classes of particles and to find and identify a particle class that may contain only 1 or 2 particles.

We are conducting an experimental program that is designed to define the limits of accuracy and precision associated with APA. Our objectives are to determine the relationships between experimental parameters, and to establish detection thresholds with subsequent identification of unique particulate groups. In addition, we will investigate the improvements, if any, obtained by applying advanced particle correction procedures to the raw x-ray data. A series of multi-element silicate glasses have been manufactured which contain varying levels of uranium ranging from about 1 to 17% by weight. These glasses are ideal for this study since they can be manufactured as bulk materials, particles with controlled shapes and particles with irregular shapes. The polished bulk materials are an ideal sample and will provide a best-case analysis. The two particle types will be used to evaluate the effects of particle shape on the accuracy and precision of APA methods. In addition, the two types of particles will be used to determine if any of the existing algorithms for quantitative particle analysis are applicable to APA, and to what extent these algorithms improve particle class separation and identification.

To date we have conducted preliminary studies of polished bulk glasses. The different bulk glasses were analyzed for three different live times, 15 s, 30 s, and 2 min. For a 2 min analysis time, the six different glasses with uranium concentrations of 1, 3, 4, 8, 10, and 17 weight percent, were correctly distinguished by a simple cluster analysis algorithm. However, at the shorter counting times the lower three and middle two concentrations were mixed and the algorithm could not distinguish among them. The results from these studies indicate that poor counting statistics cause severe problems in distinguishing the different glass concentrations, even from ideal bulk samples. Current counting times for particles by commercial/academic laboratories are as short as 1 s, with conclusions of source apportionment studies depending on these measurements. Our studies indicate that longer data collection times are required for identifying particle populations with similar element signatures but differing element concentrations.

12. Desktop Spectrum Analyzer: A Software Tool for Analysis and Simulation of Electron-Excited Energy Dispersive X-ray Spectra

C.E. Fiori, R.L. Myklebust, and C. Swyt (Guest Scientist)

Desktop Spectrum Analyzer (DTSA) is a software product for the Macintosh II class of computers developed as a joint NIST and NIH research effort and offered for sale by the NIST Office of Standard Reference Data (OSRD). DTSA provides mathematical algorithms for complete analysis of electron beam-excited x-ray spectra, as obtained from the electron probe microanalyzer, analytical scanning electron microscope, and analytical electron microscope. DTSA has four major modes of operation:

1. Direct acquisition of x-ray spectra: By using a special multi-channel analyzer board which is available for the Macintosh II, DTSA can directly acquire energy dispersive x-ray spectra (EDS). In acquiring spectra, it carries out all of the normal signal processing functions, such as deadtime correction.

2. Conversion of energy dispersive spectra from other multichannel analyzer systems: Software decoders are included to translate the file structure of spectral data formats of all known commercial multi-channel analyzers into the DTSA environment.

3. Deconvolution of spectra and quantitative elemental analysis: Spectral deconvolution for peak overlaps and background correction can be carried out by multiple linear least squares from elemental reference spectra or sequential simplex peak fitting. Quantitative elemental analysis on the characteristic intensities thus extracted can be performed with the NIST ZAF matrix correction procedure FRAME and a variety of other methods, including first principles "standardless analysis" and the Hall method for biological/polymeric materials.

4. First principles generation of x-ray spectra: Energy dispersive x-ray spectra can be simulated from first principles for either bulk or thin film materials for any mixture of elemental constituents. A variety of choices for the ionization cross section for characteristic x-ray generation and the cross section for bremsstrahlung continuum background. This theoretical spectrum is then modified for absorption within the specimen, for absorption or transmission through the components of the

x-ray spectrometer, for the spectrometer response function, and for the major spectral artifacts, such as silicon escape peaks. Finally, the spectrum is modified to reflect the true statistics of counting discrete photon capture events.

An important feature of DTSA is that it can be used to study problems involving limits of detection under practical analytical situations. "Monte Carlo" statistics spectra can be repeatedly generated and then deconvoluted with the algorithms incorporated in DTSA. The quantitative results of these deconvolution operations can be output in the form of files that are compatible with several of the major commercial statistics and graphical analysis software packages. By quantitatively studying spectra that incorporate true statistical variations, a good estimate of detection limits and accuracy can be obtained, and a strategy for analysis can be optimized. For example, the limit of detection for the analytical peak of a minor or trace constituent, in the presence of a large peak from a matrix element, can be readily studied. In most cases, homogeneous standards suitable for microanalysis are not available, especially those containing specified quantities of trace constituents. DTSA thus provides a unique tool for the analyst to attack problems from a new perspective.

13. Progress in Asbestos Standard Reference Materials

E.B. Steel, S. Turner, J. Verkouteren, J.M. Phelps, D.J. Hues, and E.S. Windsor

We have continued to support the approximately 1000 asbestos analysis laboratories through technical support for laboratory accreditation and by reissuing two Standard Reference Materials (SRM's) critical to quality assurance. The reissued standards are SRM 1876b Chrysotile Asbestos Standard and SRM 1866a Bulk Asbestos--Common. In addition, work towards issuing two new reference materials was started. These new SRMs are Bulk Asbestos--Uncommon (SRM 1867) and a set of quantitative standards for asbestos in building materials.

SRM 1866a consists of three samples of greater than 90% mine-grade asbestos. This SRM serves the community by providing reference materials for the identification of asbestos using polarized light microscopy (PLM). The polarized light optical properties of chrysotile, Amosite, and crocidolite asbestos were certified so that the laboratories could calibrate their measurement process. The accuracy and precision of the NIST refractive index measurement technique were improved for the reissue. This allowed us to identify true variation in refractive index within the fiber population for both chrysotile and Amosite asbestos. One hypothesis is that the variation in refractive index is due to the random orientation of submicrometer fibrils within the larger, measurable, fiber bundles. Preliminary refractive index measurements of SRM 1867, which is a PLM reference material for anthophyllite and actinolite/tremolite asbestos, shows a bimodal distribution of indices suggesting the possibility of random orientation.

SRM 1876b was reissued for use in the analysis of asbestos on filters by transmission electron microscopy. The materials in this SRM were generated by aerosol deposition of chrysotile fibers, in contrast to the previous SRMs and related RMs which used liquid generation and deposition.

The aerosol generation results in complex arrangements of fibers that more closely mimic real-world, air collected samples. A suite of 320 filters was loaded with asbestos by an aerosol generator at the Stanford Research Institute. More than 100 labor-intensive NIST verified analyses were performed to determine the average loading of asbestos on the filters, to characterize the homogeneity of the loading, and to determine whether the distribution of the counts was consistent with a Poisson model. The homogeneity was characterized at several levels including between-filters and within-filters. Approximately 200 SRM units were delivered to the Standard Reference Material Program.

Research into the development of a quantitative building material standard was initiated. This standard will be used to calibrate the quantitative analysis capabilities of the laboratories. We have found that the majority of laboratories typically show a large positive bias that is a function of matrix and asbestos visibility. Therefore, we have screened a variety of building materials, including floor tiles, insulation, cementitious coatings, etc., as well as quantitative aids such as microscope grain mount slides. Next, we will choose and characterize several of these materials for Standard Reference Material.

14. Femtosecond Probes of Vibrationally Excited Adsorbate Dynamics

R.R. Cavanagh, J.D. Beckerle, J.C. Stephenson (PL), M.P. Casassa (PL), and E.J. Heilweil (PL)

The rate of energy transfer in adsorbed layers has been the topic of numerous theoretical and experimental studies. A critical limitation of these efforts has been the lack of direct time-resolved measurements of these rates at well characterized surfaces. We have recently been successful in applying femtosecond laser techniques to measure directly energy transfer processes on well characterized metal single crystals. Infrared pulses have been used to follow the response of excited CO oscillators at 0.5 monolayer coverage on a Pt(111) substrate under ultrahigh vacuum conditions. In these experiments an intense infrared pump pulse of 700 femtosecond duration excites the 2106 cm^{-1} stretch mode of CO bound in top sites in the c(4x2) adlayer, and a weaker probe pulse subsequently monitors the evolution of the excited CO adlayer. To establish the full spectral response of the adlayer, the probe pulse is spectrally dispersed and analyzed with a grating spectrometer.

These measurements have demonstrated that the excited states of strongly coupled adlayers can be highly perturbed compared to their equilibrium description. As the fraction of the CO oscillators that are excited approaches 15%, the full spectral feature corresponding to the $v=0 \rightarrow 1$ transition is seen to shift progressively 7 cm^{-1} to lower frequency. At this level of excitation, the spectral properties of the adlayer are clearly distinct from those anticipated for either strongly coupled harmonic oscillators - where no shift is anticipated, or isolated anharmonic oscillators - where distinct new spectral features should emerge. These measurements indicate that for adlayers of strongly coupled anharmonic oscillators, excitation of the oscillators is delocalized through all of the equivalent binding sites.

This work has stimulated a variety of theoretical and experimental efforts to understand more fully the transient response of adlayers. From insights gained from such probes, it should become possible to combine novel laser pulse sequences with the appropriate surface reactions to achieve reaction products that would not be achievable with other methods. We plan to extend these femtosecond techniques to systems where the excited state population is generated by an intense visible pulse. In these experiments, the spectrally dispersed infrared probe will continue to be used to map out the vibrational properties of the excited adlayer. In this manner, coupling of the vibrational modes in the adlayer to electronic excitations in the substrate may be accessible. Additional measurements utilizing sum frequency generation are being initiated to investigate the transient response of optically excited surface and interface states.

15. Photoemission Studies of Fermi Surfaces

R.L. Kurtz, S.W. Robey, L.T. Hudson, S.A. Smilgys, and R.L. Stockbauer (Guest Scientist)

Photoemission has provided a wealth of knowledge regarding the electronic states of gases, solids, and surfaces. In particular, this technique has been crucial in the identification of electronic states associated with different materials and with clean and adsorbate covered surfaces. By resolving the photoemission signal as a function of incident energy and emission angle, it has become possible to probe the energies, momenta and symmetries of the electronic structure of solids. Acquisition of this angle resolved data is a laborious and time consuming task. This demand on time is not only inconvenient, but may mean that surfaces can not be maintained free of contamination for sufficiently long to make satisfactory measurements.

In this project, a novel detection technique has been developed which reduces the amount of time required to acquire the angle resolved data by approximately three orders of magnitude. By employing a display type analyzer to collect *simultaneously* data at a large number of emission angles, it is possible to map the electronic structure of crystalline materials in a fraction of the time required by more conventional techniques. Briefly, the instrument consists of an ellipsoidal-mirror electron energy analyzer to detect electron emission over a large solid angle while preserving angular information. The 2-dimensional detection is accomplished with dual microchannel plates coupled to a resistive anode encoder. This provides single-electron counting sensitivity with an analog output relating the electron emission angle with X-Y location on the detector. The crystalline azimuthal orientation is established with low energy electron diffraction which is performed with the same electron optics but using an ancillary electron gun as the excitation source.

The instrumentation required for these measurements was installed at SURF II during the past year, and initial data on the Fermi surface of Ru(001) and O/Ru(001) has now been obtained. Comparison of the acquired images with theoretically predicted Fermi surfaces for Ru indicates good qualitative agreement. The six-fold symmetry of the electronic structure is readily apparent, and the dependence on incident energy has been documented. These images provide direct information on the occupied electronic states of the bulk Brillouin zone. Studies of the nature of the Fermi surface provide data needed to understand the behavior of materials such as high-temperature superconductors and heavy fermion systems; there, the details of the Fermi surface influence parameters such as conductivity, mobility, etc.

These initial images have sufficient contrast to reveal the limitations of kinematic models to account for the full angular distribution and point to the need for a more complete multiple scattering theory. Even at this early stage, however, the technique has been able to establish the changes in electronic states which occur due to the chemisorption of oxygen on the ruthenium surface. The images that have been produced provide an immediate and direct visualization of the occupied electronic states and the relationship to bulk symmetries.

16. Product Energy Distributions Accompanying Laser-Induced Surface Reactions

S.A. Buntin and L.J. Richter

Low temperature processing of semiconductor devices offers the potential for chemically modifying device structures without causing unwanted reactions to underlying components. Laser-driven surface chemistry offers an appealing avenue for inducing these reactions, since the potential exists for the laser to deliver its energy directly to the surface-bound reactants of interest. Many of the efforts to exploit this opportunity have fallen short due to a lack of understanding of the fundamental photochemical processes that occur at even the simplest of surfaces. Previous efforts in this group have established the importance of various substrate-mediated excitation channels in model photochemical systems: hot-carrier-induced desorption on metals and surface-state-mediated photoreactions on semiconductors. Presently, the underlying mechanism of adsorbate-localized, laser-induced surface reactions are under investigation in the system $Mo(CO)_6/Si(111)$.

The photodecomposition of $Mo(CO)_6$ adsorbed on Si(111) has been examined using laser-induced fluorescence to probe the ejected CO fragments. The laser source for state-specific CO detection was implemented at NIST over the past two years. In these experiments, the $Mo(CO)_6/Si(111)$ surface is prepared under ultrahigh vacuum conditions. For $Mo(CO)_6$ coverages of 2-3 monolayers and an initial surface temperature of 100 K, 266 nm photolysis produces CO velocity distributions with two distinct components. The kinetic energies of these features correspond to 100 and 500 K. The rotational-state population distribution for each component can be characterized by a rotational temperature similar to the respective translational temperature. These different desorption channels have been (initially) interpreted in terms of a direct ejection mechanism, which gives rise to the higher energy component, and a second channel where the CO, after initial release, undergoes collisions with the surface and adlayer prior to desorption. The second channel may be important to the evaluation of potential metal deposition precursors, as 'thermal' dissociation of the collisionally accommodated CO is a mechanism for deleterious impurity incorporation into photochemically deposited films. In separate measurements, single external-reflection Fourier transform infrared spectroscopy has been explored as a complementary probe of adsorbate photochemistry on semiconductors. For the system $Mo(CO)_6/Si(111)$, we have achieved adequate sensitivity to demonstrate that the photolysis products which accumulate on the surface include at least two types of partially carbonylated $Mo(CO)_x$ species. The cross sections for the photogeneration of these two species differ significantly.

Future research further characterizing the photodecomposition of $Mo(CO)_6/Si(111)$ is planned with efforts focusing on monolayer coverages of $Mo(CO)_6$ to explore quenching due to intimate contact with the substrate. Experiments will be performed to discriminate between adsorbate-localized photochemistry, and substrate-mediated effects by probing $Mo(CO)_6$ photolysis on various substrates (including Mo and K/Si(111,)) where carriers are expected to play a more significant role than in the $Mo(CO)_6/Si(111)$ system.

17. Surfaces and Interfaces of High T_c Thin Films

S.W. Robey, R.V. Smilgys, and T.J. Hsieh (Guest Scientist)

The effective utilization of high T_c superconducting oxide materials for the fabrication of commercial devices requires the development of a viable thin film growth and processing technology. This in turn requires an understanding of the host of surface and interface related effects which emerge in any thin film device development program. Included among these are the effects of substrate surface cleanliness on film growth, chemical reactions at device interfaces during formation and subsequent annealing, and the effects of processing steps on the superconducting properties of the thin film. The focus of this project is to develop a flexible program to study fundamental aspects of these problems under well-controlled conditions. This will allow the results to be generalized to a variety of situations, rather than being confined to a specific device process.

To achieve this goal we have developed the capability to produce thin films of the superconducting oxide $DyBa_2Cu_3O_{7-x}$ under ultrahigh vacuum (UHV) conditions and study these films with a variety of spectroscopic tools, such as Auger electron spectroscopy, Reflection High Energy Electron Diffraction, and photoelectron spectroscopy. These tools will allow us to address surface and interface problems at a microscopic level and understand the driving mechanisms for the chemical interactions occurring at important device interfaces.

Over the last year we have successfully produced high T_c thin films with transition temperatures @ 85 K on MgO and $SrTiO_3$. These films are superconducting as grown and thus are suitable for investigations with the *in situ* techniques listed above. X-ray diffraction, electron microscopy, and transport measurements have been used to characterize the properties of the films after removal from the UHV system. Raman microprobe measurements have also been performed for selected samples. Auger spectroscopy has been employed for preliminary studies of MgO substrate surface preparation and of the effect of deposition conditions on the surface of the superconducting thin film.

Future work will involve continued study and optimization of deposition conditions, and further improvements to the deposition system to allow efficient use of the various surface/interface tools available. Expanded and routine use of these tools will allow the continued investigation of substrate preparation aspects and studies of the effects of vacuum conditions and processing on the metallization of high T_c oxide films. Transmission electron microscopy studies will continue primarily through our collaboration with the Superconductivty Research Center at the University of Maryland. Along with Raman microprobe measurements, we hope to investigate the effects of compositional variation on thin film growth. We will also begin to investigate growth of thin films by magnetron sputtering techniques.

18. Magnetic Engineering

W.F. Egelhoff, Jr., M.T. Kief, W.R. Bennett, and W. Schwarzacher

The objective of this project is to understand the relationship between the atomic microstructure and the magnetic properties of thin-film multilayers consisting of magnetic and nonmagnetic metals to assess present magnetic-storage devices and to engineer improved devices. A major upgrading of the experimental facilities was initiated this year. We installed an ultrahigh-vacuum surface-analysis system (consisting of measuring instruments for x-ray photoelectron [XPS], Auger electron [AES], and ion-scattering [ISS] spectroscopies) and other components. The Kerr-effect magnetic measurement system has been rebuilt for *in situ* measurements under ultrahigh vacuum conditions. A new molecular-beam epitaxy (MBE) facility has been designed with unique capabilities both for film growth and for structural analysis of the films at the atomic level. It will be the only system we know, that combines both MBE evaporators (for highly-controlled research-grade films) and magnetron sputter-guns (for industrial-production-grade films). Magnetic measurements at greatly increased field strength will be made possible by an *in situ* superconducting magnet. The facility will also have the best combination of *in situ* atomic-structural analysis techniques available anywhere (including XPS and AES diffraction, ISS, low-energy electron diffraction with spot-profile analysis, reflection high-energy electron diffraction, and scanning tunneling microscopy).

The experimental work performed this year on the existing equipment consisted of preliminary studies of Co/Pd multilayers, which are important for their potential as media for short-wavelength optical recording, and Co/Cu and Fe/Cu multilayers, which are important for their potential as magnetoresistive memory-elements in nonvolatile microelectronic chips. Progress was made on improving the Kerr rotation (signal strength) in the Co/Pd system by carefully controlled annealing to permit limited interdiffusion of Co and Pd at the interfaces. In the Co/Cu and Fe/Cu multilayer systems, progress was made in understanding which of the crystallites in the polycrystalline multilayer are responsible for its magnetoresistive properties. In the coming year, we hope to use this understanding to engineer improved properties in these multilayer systems.

19. Kinetic-Excitation Processes Produced by Ion Bombardment of Surfaces

J. Fine, J. Kolodziej (Guest Scientist), and K. Franzreb (Guest Scientist)

Ion-beam methods are widely used to investigate the structure and composition of surfaces and interfaces, but the capabilities of the methods are now limited by incomplete understanding of the fundamental collisional phenomena involved. We are investigating these phenomena which include collisional-excitation and energy-transfer events, energy states and angular distributions of ejected ions and neutrals, and bombardment-induced defect diffusion and segregation.

We have performed multiple-interaction calculations (in collaboration with Prof. M. H. Shapiro, California State Univ., Fullerton) to simulate the dynamic phenomena and atom trajectories involved when keV argon ions bombard single-crystal surfaces of aluminum, with experimental parameters corresponding to our earlier measurements. We have found, in contrast to most previous studies, that the ejection of collisionally core-excited atoms is due primarily to simple "single-collision" events between the incident ion and a target atom. To investigate these and related phenomena further, we have designed and constructed a new instrument to measure angle-resolved kinetic-energy distributions of sputtered atoms and ions and their states of excitation. Sputtered species generated by a high-intensity pulsed ion source will be detected by resonance multiphoton ionization and time-of-flight energy analysis.

We have also investigated the collisional excitation of sodium halide crystals bombarded by keV argon ions (in collaboration with Prof. M. Szymonski, Jagellonian Univ., Krakow). Measurements of the energy distributions of the resulting Auger electrons for different near-surface stoichiometries have led us to propose a new kinetic de-excitation model. According to this model, an excited sodium ion can de-excite by electron emission only through collisions with lattice halogen ions. We plan to test this model by making similar measurements with metal oxides and additional alkali halides.

20. Calculations of Electron Inelastic Mean Free Paths for Surface Analysis

C.J. Powell

The inelastic mean free path (IMFP) of low-energy electrons in solids is a crucial parameter in quantitative surface analyses by the commonly used techniques of Auger-electron spectroscopy and x-ray photoelectron spectroscopy. It is difficult, however, to measure the IMFP with the needed accuracy. In collaboration with Drs. D. R. Penn (NIST, 841) and S. Tanuma (Nippon Mining Company, Saitama, Japan), new calculations have been made of the IMFP for 50-2000 eV electrons in 27 elements and 15 inorganic compounds. We have analyzed the IMFP dependence on electron energy and on several material parameters, and have been able to develop a formula that can be used to predict IMFPs in other materials.

During the past year, we have evaluated the predictive IMFP formula from several perspectives. First, we have based our formula on an established theory of inelastic electron scattering in matter that has been shown to describe well the dependence of scattering cross sections on electron energy. Second, we have demonstrated that it would be difficult to develop an analytic formula with better accuracy. Third, we have checked the sensitivity of the computed IMFPs to the choice of parameters. Finally, we have used two powerful sum rules to check the experimental optical data used in the IMFP calculation for each material. This latter check revealed significant errors in the optical data for some of the inorganic compounds; it also was found that the predictive formula gave more reliable IMFP values than those calculated directly from the optical data. We plan to extend the IMFP calculations to other materials, initially polymers, and to perform related calculations of partial inner-shell ionization cross sections for conditions used in thin-film analysis by analytical electron microscopy.

21. Structural Properties of Thin Magnetic Films

T. Jach, M.J. Chester, and S.M. Thurgate

The magnetic properties of thin films are highly dependent on the elements involved, the structural forms they assume, and their interactions with substrates and adjoining layers through interfaces. We are applying new methods to obtain structural data that can not be easily determined by current methods. During the past year we succeeded in obtaining photoemission spectra excited by x-rays incident on substrates at grazing angles, thereby enabling us to separate the photoelectron signal due to atoms within a few atomic layers of the surface from that due to deeper atoms. Initial experiments were conducted with an optically-polished single crystal of tungsten which can be coated with adsorbates to induce surface reconstructions, and then cleaned by heating to high temperature. After measuring the penetration of adsorbates into the substrate, we intend to deposit thin nickel films which will originally assume the lattice constant of the tungsten near the interface, and then relax to the nickel lattice constant nearer the surface. We hope to be able to separate the energy levels from atoms in the two different environments.

We have applied neutron diffraction and x-ray diffraction to investigate interface formation and magnetism in transition-metal multilayers. X-ray diffraction was used to characterize the epitaxy and interface quality in Co-Au, Co-Cu, and Ni-Cu samples fabricated at the NIST and elsewhere, while grazing-angle neutron diffraction was used to measure the magnetic properties of these multilayers. The results of the neutron measurements made at the NIST reactor indicated the direction that needed to be taken to improve the structural quality of current epitaxial transition-metal magnetic films before they can be expected to demonstrate the cooperative behavior visible in epitaxial rare-earth magnetic films.

22. Theory of Surface Processes: Role of Electron Beams

J.W. Gadzuk and M.D. Stiles

A prerequisite for understanding and controlling the physical and chemical state of condensed matter surfaces and interfaces is knowledge of the electron eigenstates and resonances associated with the solid-state and atomic or molecular components of the interfacial system. Both the static ground-state characteristics as well as the dynamic properties determined by excited states can be ascertained only through procedures that require a proper set of electron wavefunctions, eigenvalues or energy bands, and excitation or response functions. Due to the central importance of electronic processes at surfaces and interfaces, we have studied the properties of directed electron beams not only as a probe of surface and interfacial properties, but also as initiators of surface reactions. The electron beams used in our theoretical studies correspond to beams from electron guns, the electron current produced in scanning tunneling microscopes (STMs), and internally generated, laser-induced hot electrons. During the past year, we have investigated ballistic-electron emission microscopy (BEEM) and resonant inelastic-electron tunneling and scattering.

BEEM is a technique, based on the STM, that is used to investigate buried interfaces. We have carried out the first "first-principles" calculation of the electron transmission across such interfaces and of the spectra expected in BEEM measurements. The systems we considered were cobalt and nickel disilicide grown on silicon, both of which are being investigated by BEEM, and are of interest because of the proposal to use these materials to make a novel type of device, the metal-base transistor. The agreement between theory and experiment for the cobalt disilicide interface was quite dramatic, while the experimental results for nickel disilicide are still preliminary.

The class of electron-induced molecular dissociation, rearrangement, and desorption processes at surfaces, which follow from the occupation of a metastable electron-resonance state, is becoming known as electron femtochemistry at surfaces due to the short-lived nature of the intermediate state responsible for the reaction. In support of experiments carried out in the Surface Dynamical Processes Group, we have developed companion theoretical models for treating a spectrum of laser-excited hot-electron processes involving the excitation of localized bonds due to transient hot-electron tunneling into and out of the resonance states associated with the localized bonds. Our theoretical excitation and desorption probabilities and translational energy distributions correspond well with the experimental data.

C. Outputs and Interactions (Surface and Microanalysis Science Division)

1. Publications

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2. Talks

Bennett, J.A., "Relative Sensitivity Factors and Useful Yields for a Microfocused Ga Ion Beam and TOF-SIMS System," American Vacuum Society 37th National Symposium, Toronto, Ontario, Canada, October 11, 1990.

Bennett, J.A., "Feasibility of Nonresonant Laser Postionization Using a Laser/Ion Microprobe Time-of-Flight Mass Spectrometer," 2nd International Workshop on Post-Ionization Techniques for Surface Analysis (PITSA '91), Pennsylvania State University, University Park, PA, April 17, 1991.

Bennett, W.R., "Concurrent Enhancement of Kerr Rotation and Antiferromagnetic Coupling in Epitaxial Fe/Cu/Fe Structures," American Physical Society, Cincinnati, OH, March 21, 1991.

Bennett, W.R., "Concurrent Enhancement of Kerr Rotation and Antiferromagnetic Coupling in Epitaxial Fe/Cu/Fe Structures," Fifth Joint Conference on Magnetism and Magnetic Materials and Intermag Conference, Pittsburgh, PA, June 19, 1991.

Bright, D.S., "Visibility of Objects in Noisy Images as a Function of Contrast, Noise Level, and Object Size," 26th Annual Conference of the Microbeam Analysis Society, San Jose, CA, August 7, 1991.

Bright, D.S., "Computer Assisted Microscopy, Quantitative Metallography - Techniques and Applications," ASM Pittsburgh Golden Triangle Chapter 1991 Educational Seminar, Pittsburgh, PA, March 19, 1991. Invited

Bright, D.S. "Concentration Histogram Imaging," ASM Pittsburgh Golden Triangle Chapter 1991 Educational Seminar, Pittsburgh, PA, March 19, 1991. Invited

Bright, D.S., "Computer Assisted Microscopy, Quantitative Metallography - Techniques and Applications," ASM Pittsburgh Golden Triangle Chapter 1991 Educational Seminar, Pittsburgh, PA, March 19, 1991. Invited

Bright, D.S., "Digital Imaging - Pratices and Pitfalls," Interdisciplinary Research Workshop on Image Analysis, Sigma Xi, Texas A&M Chapter, College Station TX, April 2, 1991. Invited

Bright, D.S., "Digital Images and Your Computer," Initiation and Awards Banquet Address, Sigma Xi, Texas A&M Chapter, College Station TX, April 2, 1991. Invited

Bright, D.S., "Scaling and Enhancement of Micrographs and X-Ray Maps for Viewing, Publication and Analysis," Scanning 91, Atlantic City, NJ, 12 April 1991.

Buntin, S.A., "State-Resolved Studies of Laser-Induced Desorption from Si(111)," American Chemical Society Meeting, Atlanta, GA, April 18, 1991.

Buntin, S.A., "Surface-State Mediated Photodesorption: NO on Si(111) 7x7," Gordon Research Conference on the Dynamics of Gas-Surface Interactions, Andover, NH, August 5, 1991.

Buntin, S.A., "UV Photolysis of Mo(CO)$_6$(g) and Mo(CO)$_6$/Si(111) 7x7 State-Resolved Studies of the CO Photofragment," Gordon Research Conference on the Dynamics of Gas-Surface Interactions, Andover, NH, August 7, 1991.

Cavanagh, R.R., "Picosecond and Femtosecond Time-Resolved Probes of Adsorbate Vibrational Relaxation," University of Toronto & Laser Center, Toronto, Canada, October 9, 1990. Invited

Cavanagh, R.R., "Time-Resolved Measurements of Vibrational Phase and Population Transients: Subpicosecond IR Pump-Probe Studies of CO/Pt(111)," American Vacuum Society Meeting, Toronto, Canada, October 10, 1990.

Cavanagh, R.R., "Laser-Induced Desorption of NO from Si(111): Coverage Dependence of Excitation Channels," American Vacuum Society Meeting, Toronto, Canada, October 10, 1990.

Cavanagh, R.R., "Time-Resolved Probes of Energy Transfer at Surfaces," University of Rochester, Rochester NY, Nov. 8, 1990. Invited

Cavanagh, R.R., "Laser Induced Desorption from Metal and Semiconductor Surfaces Probed Using State-Specific Laser Diagnostics," Xerox Corporation, Webster, NY, Nov. 9, 1990. Invited

Cavanagh, R.R., "Picosecond and Femtosecond Probing of Adsorbate Vibrations," Department of Electrical Engineering, Columbia University, New York, NY, January 29, 1991. Invited

Cavanagh, R.R., "Relaxation of Intermolecular Vibrations at Surfaces," American Physical Society Meeting, Cincinnati, OH, March 21, 1991. Invited

Cavanagh, R.R., "Time-Resolved Probes of Vibrationally Excited Adsorbed Molecules," Pacific Northwest Laboratory, Richland, WA, April 9, 1991. Invited

Cavanagh, R.R., "Time-Resolved Probes of Vibrationally Excited Adsorbed Molecules," Physical Chemistry Seminar, University of Washington, Seattle, WA, April 10, 1991. Invited

Cavanagh, R.R., "Pico- and Femtosecond Probing of Vibrational Energy Transfer at Surfaces," Twelfth European Conference on Surface Science, Stockholm, Sweden, September 9, 1991. Invited

Chi, P.H., "Quantitative Depth Profiling of Aluminum Through The Si/SiO2 Interface," Fourth SIMS East Coast Meeting , AT&T Bell Labs, Murray Hill, NJ, May 16-17, 1991.

Chi, P.H., "Quantitative Depth Profiling of Aluminum-implanted SIMOX Using Secondary Ion Spectrometry," Electron Microscopy Society of America Meeting, San Jose, CA, August 4-9, 1991.

Currie, L.A., "Plume Detection," Cocoa Beach, FL, December 4, 1990. Invited.

Currie, L.A., "Isotopic Methods of C-Source Apportionment," Research Triangle Park, NC, February 7, 1991. Invited.

Currie, L.A., "Plume Detection," Sacramento, CA, February 28, 1991. Invited.

Currie, L.A., "Improved Atmospheric Understanding Through Exploratory Data Analysis and Complementary Modeling: The Urban K-Pb-C System," Vienna, Austria, April 4, 1991.

Currie, L.A., "Apportionment of Atmospheric Particles: ^{14}C + Multivariate Chemical Data," Tucson, AZ, May 20, 1991. Invited.

Currie, L.A., "Source Apportionment of Wintertime Organic Aerosols in Boise, ID by Chemical and Isotopic (^{14}C) Methods," Vancouver, British Columbia, June 9, 1991. Invited.

Currie, L.A., "STD and the Chemical Measurement Process," NIST, Gaithersburg, MD, June 20, 1991.

Currie, L.A., "Data Structure and Quality and The Possibility of Identification," St. Louis, MO, July 10, 1991. Invited.

Currie, L.A., "In Pursuit of Accuracy: Nomenclature, Assumptions, and Standards," Chiba, Japan, August 28, 1991. Invited.

Egelhoff, Jr., W.F., "XPS and Auger Forward Scattering," Corning Research Laboratories, Elmira, NY, October 5, 1990. Invited

Egelhoff, Jr., W.F., "XPS and Auger Forward Scattering Studies of Epitaxial Growth," American Vacuum Society Meeting, Toronto, Canada, October 9, 1990. Invited

Egelhoff, Jr., W.F., "XPS and Auger Forward Scattering Studies of Epitaxial Growth," Department of Physics, University of California, Riverside, CA, October 23, 1990. Invited

Egelhoff, Jr., W.F., "XPS and Auger Forward Scattering: A New Tool for Surface Crystallography," Department of Physics, University of Texas, Arlington, TX, February 27, 1991. Invited

Egelhoff, Jr., W.F., "XPS Forward Scattering Studies of Fe on Ag(100)," American Physical Society Meeting, Cincinnati, OH, March 20, 1991.

Egelhoff, Jr., W.F., "Thickness-Dependent Magnetic and Structural Properties of Epitaxial fcc-Fe Films," American Physical Society Meeting, Cincinnati, OH, March 20, 1991.

Egelhoff, Jr., W.F., "Magnetization Measurements of Coupled, Ultrathin fcc Fe/Cu/Fe Films," American Physical Society Meeting, Cincinnati, OH, March 21, 1991.

Egelhoff, Jr., W.F., "XPS and Auger Forward Scattering Studies of the Structure of Metal-Metal Interfaces," Material Research Society Meeting, Anaheim, CA, April 29, 1991.

Egelhoff, Jr., W.F., "Oscillations in Kerr Rotation and Antiferromagnetic Coupling in Fe/Cu/Fe Epitaxial Bilayers," International Workshop on Spin Valve Layered Structures, Madrid, Spain, September 9, 1991. Invited

Etz, E.S., "The Micro-Raman Spectra of Metal Phthalocyanine Thin Films," Symposium on Vibrational Microspectroscopy, 1990 Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Cleveland, Ohio, October 10, 1990. Invited

Etz, E.S., "The Micro-Raman Spectra of Ceramic Samples and Thin Films of the Yttrium and Dysprosium Barium Cuprate Superconductor," NIST In-House-High-Tc Superconductivity Review, NIST-Gaithersburg, March 27, 1991.

Etz. E.S., "Vibrational Microspectroscopy for Materials Characterization," Symposium on Materials Science, SCANNING-'91 Meeting, joint with Third International Conference on Confocal Microscopy and Fourth International Conference on 3-D Image Processing in Microscopy, Atlantic City, New Jersey, April 11, 1991. Invited

Etz, E.S., "Micro-Raman Characterization of Impurity Phases in Ceramic and Thin Film Samples of the Y-Ba-Cu-O High-Tc Superconductor," Symposium on Optical Microprobe Spectroscopy, 1991 Joint Meeting of the Microbeam Analysis Society and the Electron Microscopy Society of America, San Jose, California, August 6, 1991. Invited

Etz, E.S., "Requirements of a Standard for the Chemical Characterization of CVD Diamond by Raman Spectroscopy," First International Conference on the Applications of Diamond Films and Related Materials, Auburn University, Auburn, Alabama, August 22, 1991.

Fine, J., "Evaluation of Sputter-Induced Interface Broadening Processes in Multilayered Materials," Sixth International Conference on Quantitative Surface Analysis, London, England, Nov. 13, 1990. Invited

Fine, J., "Collisional Excitation Trajectory Calculations for Aℓ(100)," Physics Department Seminar, University of York, York, UK, Nov. 22, 1990.

Fine, J., "A Molecular Dynamics Simulation of Collisional Excitation in Sputtered Al," Physics Department Seminar, University of York, York, England, Nov. 22, 1990. Invited

Fine, J., "Scanning Scattering Microscope: A Novel Optical Technical for Imaging Surface Microtopography," Microphysics of Surfaces: Beam-Induced Processes Topical Meeting, Sante Fe, NM, February 13, 1991.

Fine, J., "A Molecular Dynamics Simulation of Collisional Excitation in Sputtered Al," Second International Workshop on Postionization Techniques in Surface Analysis, Pennsylvania State University, University Park, PA, May 16, 1991.

Fiori, C.E., "The Use of Small Computers for Spectral and Image Analysis," Tour Talk for the Microbeam Analysis Society, Ottawa, Canada, July 1991. Invited

Fiori, C.E., "Artifacts of the Human Visual System," Tour Talk for the Microbeam Analysis Society, Beaufort, NC, September, 1991. Invited

Fiori, C.E., "The Use of Small Computers in Microscopy: A Tutorial Workshop," Electron Microscopy Society of America, San Jose, CA, August 1991.

Fletcher, R.A., Bennett, J.A., Hoeft, S., and Etz, E.S., "LAMMS and Raman Spectroscopy of Metal Phthalocyanine Particles and Films," Microbeam Analysis Society Meeting August 5, 1991.

Cleary, T.G., Fletcher, R.A., Mulholland, G.W., Ives, L.K., and Gentry, J.W., "Generation and Characterization of Acetylene Smokes," Proceedings of Chemical and Physical Processes Combustiom Meeting, Technical Eastern Section of Combustion Institute, Daytona, FL, December 4, 1990.

Gadzuk, J.W., "Wave Packet Study of Inelastic Resonant Tunneling," American Physical Society Meeting, Cincinnati, OH, March 20, 1991.

Gadzuk, J.W., "Hot-Electron Induced Desorption: Resonant Inelastic Scattering-Tunneling Revisited," American Physical Society Meeting, Cincinnati, OH, March 22, 1991.

Gadzuk, J.W., "Electron Femtochemistry at Surfaces," Physics Department Colloquium, Pennsylvania State University, State College, PA, May 7, 1991. Invited

Gadzuk, J.W., "The Semiclassical Way to Molecular Dynamics at Surfaces," Liverpool University, Liverpool, England, May 24, 1991. Invited

Gadzuk, J.W., "Inelastic Resonance Scattering, Tunneling, and Desorption," Liverpool University, Liverpool, England, May 29, 1991. Invited

Gadzuk, J.W., "Charge Transfer: A Key to Electron Femtochemistry at Surfaces," European Science Foundation Workshop on Charge Transfer Phenomena, Amsterdam, The Netherlands, May 30, 1991. Invited

Gadzuk, J.W., "Inelastic Resonance Scattering, Tunneling, and Desorption," Theoretical Solid State Physics Colloquium, Institut fur Festkorperforschung of the Forschungszentrum Julich, Julich, Germany, June 3, 1991. Invited

Gadzuk, J.W., "Electron Femtosecond Chemistry at Surfaces," Gordon Research Conference on Dynamics of Gas Surface Interactions, Andover, NH, August 6, 1991. Invited

Gillen, J.G., "Image Depth Profiling SIMS: An Evaluation for the Analysis of Light Element Diffusion in YBCO Single Crystal Superconductors," Sixth NIST Superconductivity Symposium, NIST, Gaithersburg, MD, March 26-27, 1991.

Gillen, J.G., "Gelatin Films as Standards for Quantitative Molecular SIMS Analysis of Biological Tissues," 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19-24, 1991.

Gillen, J.G., "Macintosh Based SIMS Image Processing," 4th East Coast Workshop on Secondary Ion Mass Spectrometry," AT&T Bell Labs, Murray Hill, NJ, May 16,17 1991.

Gillen, J.G., "Quantitative 3D SIMS Imaging Using the Ion Microscope," 8th International Conference on Secondary Ion Mass Spectrometry, Amsterdam, Netherlands, September 13, 1991.

Hudson, L.T., "A Resonant Photoemission and Core-Level Study of BaTiO3," American Physical Society Meeting, Cincinnati, OH, March 22, 1991.

Jach, T., "Theory of X-Ray Standing Waves in the Grazing Angle Geometry," American Physical Society Meeting, Cincinnati, OH, March 20, 1991.

Jach, T., "Grazing Angle X-Ray Photoemission," Gordon Research Conference on X-Ray Physics, New London, NH, August 15, 1991.

Klouda, G.A., "Source Approtionment of Wintertime Organic Aerosols in Boise, ID, by Chemical and Isotopic (^{14}C) Methods," Vancouver, British Columbia, June 9, 1991. Invited.

Klouda, G.A., "Radiocarbon Source Apportionment of Atmospheric Aerosols for Boise, ID," Tucson, AZ, May 23, 1991.

Kurtz, R.L., "Photoelectron Imaging of Electronic Structure: Ru(0001)," American Physical Society Meeting, Cincinnati, OH, March 21, 1991.

Kurtz, R.L., "Photoelectron Imaging of Bands and Bonds Using Synchrotron Radiation," Department of Physics, Louisiana State University, Baton Rouge, LA, April 25, 1991. Invited

Kurtz, R.L., "Photoelectron Imaging of the Electronic Structure of Clean and Adsorbate Covered Ru(0001)," Fifty-First Annual Conference on Physical Electronics, Rutgers, The State University, Piscataway, NJ, June 17, 1991.

Marinenko, R.B., "Digital Mapping with Electron Beam Instruments," SCANNING 91 Meeting, Atlantic City, NJ, April 1991.

Marinenko, R.B., "Analysis of High T_c Bulk Superconductors with Electron Microprobe Compositional Mapping," 26th Annual Meeting of the Microbeam Analysis Society, San Jose, CA, August 1991.

Myklebust, R.L., "Monte Carlo Electron Trajectory Simulation of the Depth Sensitivity of Electron Backscattering," Microbeam Analysis-1991, San Jose, CA, August 8, 1991. Invited

Myklebust, R.L., "Image Processing, Spectral Processing and Programming Tools on the Macintosh Computer," Scientific Computing and Automation Conference, Philadelphia, PA, September 24, 1991. Invited

Newbury, D.E., "New Tools for Elucidating the Chemical Microstructure of Matter: Compositional Mapping and Computer-Aided Analysis," Keynote Paper, Materials Characterization Conference and Exposition, United Technologies Research Center, East Hartford, CT, October 23, 1990. Invited

Newbury, D.E., "Microanalysis to Nanoanalysis: Measuring Composition at High Spatial Resolution," Technical Symposium, Materials Science and Engineering Centennial Celebration, Lehigh University, Bethlehem, PA, Nov. 2, 1990. Invited

Newbury, D.E., "An Updated Overview of Chemical Characterization for High TcSuperconductors at NIST," NIST Superconductivity Program Review, Mar. 27, 1991. Invited

Newbury, D.E., "Elemental Analysis in the SEM and TEM", American Society for Metals, NIST, May 29, 1991. Invited

Newbury, D.E., "Compositional Mapping with the Electron Probe Microanalyzer: Capabilities, Limitations, Opportunities," Electron Microscopy Society of America Presidential Symposium, 49th Annual Conference, San Jose, CA, August 5, 1991. Invited

Newbury, D.E., "Monte Carlo Electron Trajectory Simulation for Electron Probe Analysis: Present Utility and Future Possibilities," Microbeam Analysis Society Presidential Symposium, 25th Annual Conference, San Jose, CA, August 5, 1991. Invited

Newbury, D.E., "Lateral Profiling of Solute Depletion in Al-Li Alloys by SIMS," Secondary Ion Mass Spectrometry VIII, Amsterdam, The Netherlands, September 18, 1991.

Phelps, J.M., "Asbestos in Schools," National Institute of Standards and Technology, Public Open House, Fall 1991.

Powell, C.J., "Electron Inelastic Mean Free Paths in Compounds for Energies Between 50 and 2000 eV," American Vacuum Society Meeting, Toronto, Canada, October 9, 1990.

Powell, C.J., "Electron Inelastic Mean Free Paths in Compounds for Energies Between 50 and 2000 eV," Sixth International Conference on Quantitative Surface Analysis," London, England, Nov. 14, 1990.

Powell, C.J., "Formal Data Bases: The Current Situation and Future Trends," Sixth International Conference on Quantitative Surface Analysis, London, England, Nov. 15, 1990. Invited

Powell, C.J., "Progress in Quantitative Surface Analysis by AES and XPS: The Role of Matrix Factors," Perkin Elmer-Physical Electronics Division, Eden Prairie, MN, February 27, 1991. Invited

Powell, C.J., "Experimental and Theoretical Determinations of Electron Attenuation Lengths and Inelastic Mean Free Paths for Surface Studies," Institute of Physics Seminar, Jagellonian University, Krakow, Poland, May 15, 1991. Invited

Powell, C.J., "Progress and Pitfalls in Quantitative Surface Analysis by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," Institute of Physics Seminar, Jagellonian University, Krakow, Poland, May 16, 1991. Invited

Powell, C.J., "Inelastic Mean Free Paths of Low-Energy Electrons in Solids," Fifteenth International Seminar on Surface Physics, Przesieka, Poland, May 22, 1991. Invited

Powell, C.J., "X-Ray Photoelectron Spectroscopy," Short Course on Microanalysis of Electronics Organized by ASM International, National Institute of Standards & Technology, Gaithersburg, MD, May 29, 1991. Invited

Powell, C.J., "Auger-Electron Spectroscopy," Short Course on Microanalysis of Electronics Organized by ASM International, National Institute of Standards & Technology, Gaithersburg, MD, May 30, 1991. Invited

Powell, C.J., "Comparison of Measured and Calculated Appearance-Potential Spectra for Six 3d Metals," International Workshop on Auger Spectroscopy and Electronic Structure, Malmo, Sweden, September 4, 1991.

Powell, C.J., "Recent Advances and Future Opportunities in Auger Electron Spectroscopy," Workshop on Auger Spectroscopy and Electronic Structure, Malmo, Sweden, September 6, 1991. Invited

Richter, L.J., "Laser-Induced Desorption of NO from Si(111): Coverage Dependence of Excitation Channels," American Vacuum Society Meeting, Toronto, Canada, October 11, 1990.

Richter, L.J., "State-Specific Studies of the Laser-Induced Desorption of an NO from Si(111)," Microphysics of Surfaces: Beam-Induced Processes Topical Meeting, Sante Fe, NM, February 11, 1991.

Richter, L.J., "State-Specific Studies of the Laser-Induced Desorption," Sandia National Laboratories, Albuquerque, NM, February 14, 1991.

Simons, D.S., "Secondary Ion Mass Spectrometry A Tutorial," Electronic Science and Technology Division Seminar, Naval Research Laboratory, Washington, DC, March 8, 1991. Invited

Simons, D.S., "Compositional Mapping," NIST Visiting Committee Meeting, NIST Lab, Boulder CO, June 11, 1991. Invited

Simons, D.S., "SIMS as a Diagnostic Tool for Ion Implantation and Molecular Beam Epitaxy," Microbeam Analysis Society, San Jose, CA, August 9, 1991. Invited

Simons, D.S., "SIMS Analysis of Fused Clay Microspheres Containing Plutonium," Eighth International Conference on Secondary Ion Mass Spectrometry, Amsterdam, The Netherlands, September 19, 1991.

Small, J.A., "Electron Probe Compositional Mapping of Particles and Samples with Irregular Surfaces," Microbeam Analysis Society, San Jose, CA, August 1991,

Stiles, M.D., "Coulomb Blockade Effects in Single Tunnel Junctions," Departments of Physics and Astronomy, University of Maryland, College Park, MD, December 3, 1990. Invited

Stiles, M.D., "Electron Transmission Through Interfaces," Workshop on Computational Condensed Matter Physics," Trieste, Italy, January 17, 1991. Invited

Stiles, M.D., "Ballistic Electron Emission Microscopy Theory for $NiSi_2/Si(111)$," 2nd Ballistic Electron Emission Microscopy Workshop, Pasadena, CA, January 28, 1991.

Stiles, M.D., "Theory of Ballistic Electron Emission Spectroscopy for $NiSi_2/Si(111)$ and $CoSi_2/Si(111)$ Interfaces," Physics and Chemistry of Semiconductor Interfaces Conference, Long Beach, CA, January 31, 1991.

Stiles, M.D., "Electron Transmission Through Interfaces," Department of Physics, Indiana University, Bloomington, IN, February 15, 1991. Invited

Stiles, M.D., "Coulomb Blockade Effects in Single Tunnel Junctions," Department of Physics, Ohio State University, Columbus, OH, February 18, 1991. Invited

Stiles, M.D., "Single Electron Charging Effects in Driven Tunnel Junctions," American Physical Society Meeting, Cincinnati, OH, March 21, 1991.

Turner, S., Doorn, S.S, Phelps, J.M., Windsor, E.S., Steel E.B., and Beard M.E., "Large-scale Interlaboratory Study of the Accuracy of Asbestos Analysis by TEM," Electron Microscopy Society of America Meeting, San Jose, CA, August 7, 1991. Invited

Verkouteren, R.M., "Relationships Among CO_2, CO, CH_2 and H_2 During Reduction of CO_2 to Graphitic Carbon on Iron Wool," Tucson, AZ, May 21, 1991.

Verkouteren, R.M., "Design of a Thermal Diffusion Micro-Column for ^{14}C Enhancement of Carbon Monoxice," Tucson, AZ, May 21, 1991.

Velapoldi, R.A., "NIST Update," Contractors Meeting, Cocoa Beach, FL, January 30, 1991.

Velapoldi, R.A., "Program Overview," Contractors Meeting, Cocoa Beach, FL, June 20, 1991.

Velapoldi, R.A., "Chemistry Research in CSTL," to University of Virginia students at NIST, Gaithersburg, MD, July 7, 1991.

Wight, S.A., Divita, F., Ondov, J.M., "Analysis of Particles Collected by Micro-orifice Uniform Deposit Impactor from the Philadelphia Area," Poster Presentation at the 21st International Symposium on Environmental Analytical Chemistry, Jekyll Island, Georgia, May 20, 1991.

Wight, S.A., "Research in Analytical Scanning Electron Microscopy," University of Maryland, Chemistry Department Seminar, College Park, Maryland, October 26, 1990.

3. Committee Assignments

D.S. Bright

ASTM E-29 Particle Size Measurement
ASTM E-29.04 Liquid Particle Measurement

R.R. Cavanagh

Elected vice-chair of Gordon Research Conferences - Dynamics of Gas/Surface Interactions ('93)
NIST 25/90th Anniversary Symposium Committee

L.A. Currie

Titular member, IUPAC Commission V.1 (General Aspects of Analytical Chemistry)
IUPAC Working Group on Chemometrics
Member of IUPAC Commission on Environmental Analytical Chemistry
The Chemometrics Award Committee of the American Statistical Association
RPP Panel, AFTAC
Commission on Environment Analytical Chemistry
International Radiocarbon Conference on "Environmental Science" (Chairman)
Lead, Technical Issues (AFTAC-QA)
NSF Advisory Panel for WHOI Accelerator Laboratory (Chairman)
American Statistical Association, Committee for the "Chemostatistics Award"
NIST Consultative Group for ISO/TAG4 Working Group on "Guide to the Expression of Uncertainty in Measurement"
CSTL Long-range planning committee on "Process Modeling and Simulation"
Advisory Editor, CRC Press "Chemometrics Series"
IAEA: Multivariate Exploration of Data Structure and Quality
ANSI Committee and Yankee Atomic Electric Co., State of Arizona

D.L. Duewer

North American Chapter of the International Chemometrics Society (Secretary)

E.S. Etz

ASTM E-13 Molecular Spectroscopy
ASTM E-13.08 Raman Spectroscopy
ASTM D-22 Sampling and Analysis of Atmospheres

J. Fine

Sub-committee on Standard Reference Materials, ASTM Committee E-42 on Surface Analysis (Chairman)

R.A. Fletcher

IES Working Group 014 - Calibration of Airborne Particle Counters

J.W. Gadzuk

- Advisory Editorial Board, "Progress in Surface Science"
- International Advisory Committee, 7th International Conference on Vibrations at Surfaces
- CSTL Colloquium Committee
- NIST Information Resource Center (Subject Specialist Consultant)

G.A. Klouda

- Division 837 Safety Committee
- City of Albuquerque (^{14}CO study)

R.B. Marinenko

- Microbeam Analysis Society (Director)

R.L. Myklebust

- ASTM E-2 Emission Spectroscopy
- ASTM E-2.04 Standard Reference Material

D.E. Newbury

- ASTM E-42 Surface Analysis
- Journal of Microscopy, Editorial Review Board
- Scanning, Editorial Review Board
- J. Trace and Microprobe Techniques, Editorial Review Board
- CSTL Colloquium Series (Co-chairman)

C.J. Powell

- ASTM Committee E-42 on Surface Analysis (Immediate Past Chairman)
- Executive Committee; and International Liaison
- Surface Chemical Analysis Technical Working Area, Versailles Project on Advanced Materials and Standards (US representative and Vice-Chairman)
- Applied Surface Science Division, International Union of Vacuum Science, Technique, and Applications (Chairman)
- Co-opted Subcommittee on Surface Analysis, Commission V.2 on Microchemical Techniques and Trace Analysis, International Union of Pure and Applied Chemistry
- Program Committee, 12th International Vacuum Congress and 8th International Conference on Solid Surfaces
- International Program Committee and Advisory Board, Second International Workshop on Auger Spectroscopy and Electronic Structure
- Scientific Committee, European Conference on Applications of Surface and Interface Analysis (ECASIA-91)
- Organizing Committee, 4th Topical Conference on Quantitative Surface Analysis (Chairman)
- Editorial Board, "Applications of Surface Science"
- Editorial Board, "Surface and Interface Analysis"

Editorial Board, "Methods of Surface Characterization"
Editorial Board, "Journal of Electron Spectroscopy"
Editorial Board, "Surface Science Spectra"

D.S. Simons

ASTM E-42 Surface Analysis
ASTM E-42.06 Secondary Ion Mass Spectrometry
ASTM E-42.09 Standard Reference Material

J.A. Small

Microbeam Analysis Society (Secretary)
ASTM D-22 Sampling and analysis of Atmospheres

E.B. Steel

ASTM D-22 Sampling and Analysis of Atmospheres
ISO/TC 146/SC3/WGI International Standards Organization Committee

R.A. Velapoldi

ASTM E-11 on Statistical Methods
ASTM E-13 on Molecular Spectroscopy
ASTM E-13.06 on Molecular Luminescence
ASTM E-13.06.01 on Presentation of Corrected Fluorescence Spectra
ASTM E-13.06.02 on Recommended Practices on Molecular Fluorescence Spectroscopy
DoE Review Committee
Long-range Strategic Committee on Surface Interface and Microstructure Characterization (Chair)

4. Others

a. Seminars

October 23, 1990*

A. Hubert, University of Erlangen, Erlangen, Germany, "Theory and Observation of Domain Walls at Surfaces and Interfaces of Coupled Ferromagnetic Films." (Sponsor: D. Pierce)

November 29, 1990

J. Van Puymbroeck, Chemistry Department, University of Antwerp, Antwerp, Belgium, "Chemical Characterization Using Electron Energy Loss Spectroscopy (EELS) and Electron Spectroscopic Imaging (ESI)." (Division Sponsor: D.S. Simons)

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* Interface Science Seminar Series

November 29, 1990

E.F. Skelton, Naval Research Laboratory, Washington, DC, "X-Ray Diffraction From Microscopic Samples." (Division Sponsor: D. Newbury)

December 5, 1990

B.H. Cooper, Physics Department, Cornell University, Ithaca, NY, "Ion-Surface Interactions and Scattering Dynamics." (Division Sponsor: J.W. Gadzuk)

January 9, 1991*

D.W. Goodman,, Texas A&M University, College Station, TX, "Modified Chemistry at Monolayer Metal Sources." (Division Sponsor: W.F. Egelhoff, Jr.)

January 14, 1991*

K.L. Mittal, IBM Corporation, Thornwood, NY, "Adhesion Measurements of Films and Coatings: A Critical Assessment." (Sponsor: T. Nguyen)

February 8, 1991

J.M. Rowe, Reactor Radiation Division, NIST, "The NIST Cold Neutron Research Facility." (Division Sponsor: D. Newbury)

March 5, 1991*

M.G. Lagally, University of Wisconsin, Madison, WI, "Scanning Tunneling Microscopy Studies of the Initial Stages of Growth at Surfaces." (Sponsor: D. Pierce)

March 6, 1991*

U. Landman, Georgia Institute of Technology, Atlanta, GA, "Simulations of Materials from Electrons to Friction." (Division Sponsor: J.W. Gadzuk)

March 11, 1991

M. Grasserbauer, Institute for Analytical Chemistry, Technical University of Vienna, Vienna, Austria, "Recent Developments in Quantitative Secondary Ion Mass Spectroscopy." (Division Sponsor: C.J. Powell)

March 12, 1991

D.L. Duewer, St. Louis, Missouri, "A Chemometrics Approach to Structure/Function Relationships." (Division Sponsor: L.A. Currie)

March 15, 1991

C.K.N. Patel, AT&T Bell Laboratories, Murray Hill, NJ, "Materials for Electronics and Photonics." (Division Sponsor: D. Newbury)

March 27, 1991

M.J. Chester, Rutgers, The State University, Piscataway, NJ, "Atomic Structure and Vibration Studies of Metal Induced Reconstructions on Si(111) Using Medium Energy Ion Scattering." (Division Sponsor: T. Jach)

April 9, 1991

J.H. Campbell, Stanford Research Institute, Stanford, CA, "Stimulated Desorption of Neutrals as a Real-Time Probe of Chemistry on Surfaces: Reactions of CO and CH_3OH with Ni(110)." (Division Sponsor: L.J. Richter)

April 11, 1991

S. Holloway, University of Liverpool, Surface Science Research Center, Liverpool, England, "Topics on a Time Dependent Quantum Approach to Gas-Surface Reaction Dynamics." (Division Sponsor: J.W. Gadzuk)

April 16, 1991

P. Northover, Department of Materials, University of Oxford, Oxford, England, "Metallography and Microanalysis in the Study of Prehistoric Non-Ferrous Metals." (Division Sponsor: D. Newbury)

April 26, 1991

N. Jennett, H.H. Wills Physics Laboratory, University of Bristol, Bristol, England, "Epitaxial Growth, Structural Characterization, and Magnetic Properties of Ni/Fe Multilayers on Cu(111)." (Division Sponsor: W.F. Egelhoff, Jr.)

May 3, 1991*

J. Mathon, City University, London, England, "Theory of Oscillatory Exchange and Giant Magnetoresistance in Magnetic Multilayers." (Sponsor: D. Pierce)

May 15, 1991

A. Vertes, Chemistry Department, University of Antwerp, Antwerp, Balgium. "Analytical Applications of Laser-Solid Interaction." (Division Sponsor: R. Fletcher)

May 20, 1991*

S. Chiang, IBM Research Division, Almaden Research Center, San Jose, CA, "Imaging Molecules and Metals on Metal Surfaces by Scanning Tunneling Microscopy." (Division Sponsor: R. Cavanagh)

May 30, 1991*

G.E. McGuire, Microelectronics Center of North Carolina, Research Triangle Park, NC, "Characterization of Silicides for Submicron C-MOS Devices." (Division Sponsor: C.J. Powell)

June 3, 1991

U. Saffiotti, National Institutes of Health, Bethesda, MD, "Biological Assays of Crystalline Silica Samples: Surface Reactivity, DNA Damage, Toxicity, Mutation and Neoplastic Cell Tranformation." (Division Sponsor: R.A. Velapoldi)

June 7, 1991

A. Robock, Department of Meterology, University of Maryland, College Park, MD, "Global Warming: Sunbathing at Point Barrow in 2050?" (Division Sponsor: E.B. Steel)

June 14, 1991*

N. Lang, IBM Watson Research Center, Yorktown Heights, NY, "Theoretical Studies of Single Adsorbed Atoms in the Scanning Tunneling Microscope." (Sponsor: R. Celotta)

June 24, 1991*

R.J. Hamers, University of Wisconsin, Madison, WI, "Optically-Excited Scanning Tunneling Microscopy of Semiconductor Materials." (Sponsor: R. Celotta)

July 1, 1991

V.N. Ageev, A.F. Ioffe Physico-Technical Institute, Leningrad, USSR, "Electron-Stimulated Desorption of Alkali Metals from O or Si Monolayer-Covered W Surfaces: New Ideas about Mechanisms." (Division Sponsor: R.L. Kurtz)

August 1, 1991*

M. Scheffler, Fritz-Haber-Institut, Berlin, Germany, "Theory of Alkali Adsorption on Semiconductor and Metal Surfaces." (Sponsor: J. Stroscio)

September 1, 1991*

D.L. Allara, Pennsylvania State University, University Park, PA, "Molecular Monolayers: New Directions in Structure." (Sponsor: T. Nguyen)

b. Conferences/Workshops Sponsored/Co-Sponsored

November 8-9, 1991

4th Topical Conference on Quantitative Surface Analysis, Eatonville, WA

c. Faculty Appointment

R.L. Kurtz

Adjunct Associate Professor of Physics and Astronomy, Louisiana State University, Baton Rouge, LA

d. SRM Activities

1866, Bulk Asbestos
1866a, Asbestos

e. NIST Standard Reference Ozone Photometer

Company or Organization

- Boeing Company
- Xerox Corporation
- Dept. of Air Force
- NOAA
- Xerox Corporation
- Environment Canada
- NIST - SRP #0
- EPA - SRP #7

ThERMOPhYSICS

VIII. Thermophysics Division (838)

Richard F. Kayser, Chief

A. Division Overview

The Thermophysics Division is a world leader in three areas of research: the thermophysical properties of fluids and fluid mixtures, the thermophysical properties of solids at high temperatures (above 1500 K), and the measurement of pressure and leak rate. The thermophysical properties of fluids and fluid mixtures are essential to the well-being of the chemical and related industries to ensure equity in trade, innovation in process design and control, and improvements in equipment performance. The properties of solids at high temperatures play a key role in designing and fabricating high-performance materials for use in spacecraft and nuclear reactors. Accurate measurements of pressure and leak rate are essential in semiconductor processing, space simulation testing, weapons component manufacturing, and food and pharmaceutical processing.

In the fluid properties area, the Division performs experimental and theoretical research and computer simulation studies of the equilibrium, transport, and interfacial properties of pure fluids and fluid mixtures. The experimental research involves developing new, state-of-the-art measurement techniques and providing highly accurate thermophysical properties data for carefully selected pure fluids and fluid mixtures. The fluids studied are representative of broad classes of fluids and materials encountered in many industries. In synergism with the experimental programs, the Division critically evaluates and correlates thermophysical properties data and conducts research on fundamental theoretical models, new concepts and phenomena, and predictive algorithms. The results of these efforts appear as conventional correlations and tables, and more recently, as predictive computer codes.

In the area of high-temperature solids, the Division develops millisecond and microsecond techniques to measure the thermophysical properties of solids under conditions where conventional steady-state methods fail. Materials studied include high-temperature electrical conductors and metallic composites. Important products of this research include reliable thermophysical properties data and high-temperature Standard Reference Materials.

In the area of pressure, the Division performs research on the basic physical processes that underlie the measurement of pressure, partial pressure, and leak rate. The goals are to develop new and more accurate measurement methods and concepts (e.g., pressure fixed points), and to improve the U.S. national measurement standards for pressure and leak rate. In pursuit of these goals, the Division conducts research on pressure and vacuum instrumentation, including piston gages, manometers, capacitance diaphragm gages, ionization gages, spinning rotor gages, and partial pressure analyzers. The Division performs calibration and special test services for pressure (from 10^{-7} to 10^{9} Pa) and leak rate (from 10^{-14} to 10^{-8} mol/s). The Division also offers training courses on the measurement of pressure and leak rate, and interacts strongly with industry and other national laboratories to improve the accuracy of pressure and leak rate measurements throughout the U.S.

The Division consists of five groups: the Properties of Fluids Group, W.M. Haynes, Group Leader; the Fluid Science Group, M.R. Moldover, Group Leader; the Subsecond Thermophysics Group, A. Cezairliyan, Group Leader; the Pressure Group, C.D. Ehrlich, Group Leader; and the Vacuum Group, C.R. Tilford, Group Leader. The Properties of Fluids Group and Fluid Science Group are responsible for the Division's programs on the thermophysical properties of fluids and fluid mixtures, which represent close to two-thirds of the Division's total effort; the Subsecond Thermophysics Group is responsible for the program on solids at high temperatures, which represents less than 10% of the Division's effort; and the Pressure and Vacuum Groups are responsible for the programs on pressure and leak-rate measurements and standards, which represent one-third of the Division's effort. The Division has one Senior NIST Fellow, J.H.M. Levelt Sengers, and two NIST Fellows, R.D. Mountain and H.J.M. Hanley. The Properties of Fluids Group is located in Boulder, Colorado, whereas the other groups are located in Gaithersburg, Maryland.

The Division receives approximately 40% of its funds from Congressional appropriations, 50% from other agencies and organizations, 5% from the NIST Standard Reference Data Program, and 5% from calibrations in the areas of pressure and leak rate. The Division provides technical and advisory services to the Department of Energy (several offices), the Department of Defense (all branches), the National Aeronautics and Space Administration, the Environmental Protection Agency, Sandia National Laboratory, the Johns Hopkins Applied Physics Laboratory, the Gas Research Institute, the Gas Processors Association, the Electric Power Research Institute, the Air Conditioning and Refrigeration Institute, and individual firms. The Thermophysics Division may be the only division at NIST that contributes to the three principal technology transfer programs of NIST: the Standard Reference Data Program, the Standard Reference Materials Program, and the Physical Measurements Services Program.

During FY 1991, the Thermophysics Division decreased from approximately 65 full-time employees to approximately 60 full-time employees. Contributing to this decrease were the retirements of several staff members and the departures of several others, including Dr. J.F. Ely, who had been the Group Leader of the Theory of Fluids Group. One of the consequences of Dr. Ely's departure was the merger of the Theory of Fluids Group and the Properties of Fluids Group. This merger has enhanced even more the high level of synergism that already existed between the theoretical and experimental programs. Several factors were responsible for the decrease in the size of the Division, but the most important is that the cost of labor has increased annually without corresponding increases in base support. This situation has led to the reprogramming of funds from lower-priority areas to higher-priority areas. Independent of this, the Division is continually seeking new sources of support to initiate programs in important new areas.

The Division has been engaged for several years in a Congressionally-mandated program to measure and predict the thermophysical properties of chlorofluorocarbon (CFC) alternatives. This program is part of the world-wide effort to replace CFCs with non-ozone-depleting alternatives by the year 2000. CFCs are pervasive in modern society as working fluids in small and large-scale heating and cooling equipment, as blowing agents in the production of foams and insulations, and as solvents and degreasers. The objectives of the Division's program are to acquire high-accuracy thermophysical properties data for promising alternative refrigerants and refrigerant mixtures, and to develop microcomputer-based models to predict these thermophysical properties. These data and models are essential to screen mixtures for diverse applications, to implement the new fluids in existing equipment, and to design and optimize new equipment. The most promising alternative refrigerants include incompletely halogenated ethane and methane-based compounds with little or no chlorine, and mixtures of such compounds.

The Division conducts research on a number of other important fluids, including natural gas mixtures, air, water, and aqueous solutions. In the area of natural gas mixtures, the Division has been engaged in a comprehensive research program with the Gas Research Institute for nearly two decades. The objectives of this work are to provide the natural gas industry and the rate payer with the validated property data and models needed for custody-transfer transactions, and for the design, control, and energy optimization of gas processes. With regard to air, the Division recently completed a five-year experimental, correlational, and theoretical project to reduce the uncertainties in the low-temperature properties of air. The Division initiated this effort for the U.S. Air Force to support the development of an air-breathing hypersonic aerospace vehicle (the National Aerospace Plane). With regard to water, the Division is involved in a major international effort to develop both a new scientific formulation and a new industrial formulation for the thermophysical properties of water and steam. The new scientific formulation will replace the internationally accepted "NBS Steam Tables" developed in the Division in the early 1980s.

As another major activity, the Division maintains the Fluid Mixtures Data Center and the Polar Fluids Data Project for the Standard Reference Data Program. The Fluid Mixtures Data Center provides timely technology transfer of thermophysical properties data and models to the chemical process industries. The data center compiles and evaluates data on the thermodynamic and transport properties of fluids and fluid mixtures, and produces such well-known microcomputer data bases as MIPROPS and DDMIX. Most recently, the Fluid Mixtures Data Center has developed the computer package, SUPERTRAPP, which enables the user to calculate phase equilibria, single-phase properties, and transport properties for 116 pure fluids and fluid mixtures with as many as 20 components. The Polar Fluids Data Project covers the Division's efforts on water, steam, and aqueous systems, including the international efforts to develop new formulations of the thermophysical properties of water and steam. The Polar Fluids Data Project is also responsible for the predictive computer package, REFPROP, which enables the user to predict the thermophysical properties of a large number of alternative refrigerants and refrigerant mixtures. MIPROPS, DDMIX, SUPERTRAPP, and REFPROP are all available from the NIST Standard Reference Data Program.

During the past year, the Division initiated a new five-year project with the Department of Energy to construct eight new thermophysical properties apparatus. This program is the continuation of an effort begun in the early 1980s to improve the thermophysical property measurement capabilities of the U.S. The new apparatus will extend the existing state of the art for property measurements and make it possible to study complex fluid systems that are inaccessible at present, including highly polar, electrically conducting, and reactive fluids. The measurement capabilities under development include new apparatus for transport properties, thermodynamic properties, phase equilibria properties, and dielectric properties.

In the area of solids at high temperatures, the Division recently completed measurements of the heat of fusion of tungsten, which has the highest melting point (~3700 K = 6200°F) among the metals. The Division also completed a novel, high-speed, one-dimensional spatial scanning pyrometer and used it to demonstrate the feasibility of a new high-temperature technique to measure thermal conductivity. Important future directions for this program include extensions to new properties, especially mechanical properties, and the development of techniques for simultaneous measurements at high temperatures and high pressures.

The Division has made a conscious effort to increase the level of effort devoted to pressure metrology near and above atmospheric pressure. In that connection, the Division has completed the first year of a three-year project for the U.S. Air Force and the Calibration Coordination Group of the Department of Defense. The objectives are to understand and quantify the effects of using different gases and different modes of operation (i.e., absolute mode versus gage mode) on the measurement of pressure with gas-operated piston gages. The initial emphasis of the work has been on the development of two new apparatus, a three-piston-gage apparatus (TPGA) and a dynamic piston gage apparatus (DPGA). The TPGA will make it possible to use two piston gages to study a third with different gases and with modes of operation that vary continuously from absolute mode to gage mode. The DPGA will make it possible to study the dynamic response of the gages, which will provide detailed information on the forces exerted on the walls of the piston by the gas in the narrow annulus between the piston and its cylinder.

In the area of pressure measurements near and below atmospheric pressure, the Division has completed a new orifice-flow primary pressure standard that includes the transition range of pressures (0.1 to 10 Pa) where the mean free path in the gas is comparable to the orifice diameter (of the order of 1 cm). The new standard fills a gap in NIST's primary pressure standards where many important industrial processes operate, including sputtering and plasma processing of semiconductors, freeze drying of food, and superalloy casting. Efforts are underway to extend the range of the standard to higher pressures by replacing the orifice with an array of 4900 laser-drilled holes, 3-5 micrometers in diameter. When completed, the new standard will be capable of rapid and flexible operation in calibration services over the range from 10^{-4} to 10^{2} Pa. The Division has also initiated a long-term program to make accurate measurements of low-density water vapor (pressures from 10^{-5} to 10^{-2} Pa). Water is a ubiquitous contaminant in vacuum systems, and accurate measurements are of interest in the processing of semiconductor materials and in the outgassing of satellite components in space systems. After the Division completes its new primary standard source for water vapor, it will use the source to characterize the performance of vacuum gages with water vapor. Ultimately, the Division may calibrate vacuum gages for use with water.

The Division has identified several areas important for the future. As part of the NIST initiative process, the Division has proposed new programs on CFC Alternatives, Structure-Based Modeling, Partial-Pressure Measurements, Spreading of Thin Fluid Films, and Measurements Related to the Growth and Control of Semiconductor Films. The Division will intensify its efforts in the area of CFC Alternatives in response to the revised version of the Montreal Protocol adopted in London in June, 1990, and in response to the 1990 Amendments to the Clean Air Act. Both the revised protocol and the amendments indicate that eventually it will be necessary to replace even HCFCs (incompletely-halogenated chlorine-containing CFCs). The program on Structure-Based Modeling would involve the development of techniques for estimating a wide range of chemical and physical properties based on molecular-structural information alone. This program would be a collaborative effort with the Chemical Kinetics and Thermodynamics Division. The program on Partial-Pressure Measurements would involve the development of improved ion sources and new experimental techniques (e.g., multiphoton ionization) to characterize low-pressure gaseous mixtures. The emphasis would be on mixtures that contain gases that are difficult to measure with existing techniques (e.g., oxygen, carbon monoxide, and water). The program on the Spreading of Thin Fluid Films would involve the use and development of techniques such as atomic force microscopy and scanning-imaging ellipsometry to study the occurrence, thickness, and motion of thin fluid films on well-characterized organic and inorganic surfaces. This program would expand on the Division's expertise in wetting layers and wetting phase transitions. Finally, the program on Measurements Related to the Growth and Control of Semiconductor Films would involve the use and development of non-intrusive techniques such as laser-induced fluorescence and electron-impact fluorescence to measure the densities of active semiconductor gases for the purpose of evaluating and calibrating process instrumentation. In addition to these areas, the Division is considering several topics as potential competence projects. Optical Measurements of Low-Density Gases would build upon promising preliminary results obtained using resonance enhanced multiphoton ionization and infrared absorption. Complex Fluid Systems in Non-Equilibrium States would capitalize on the Division's very successful neutron-scattering program for fluids under shear. Finally, the Division has initiated several projects that will become increasingly important in the environmental area. One project involves measuring the properties of trace constituents in natural gas, whereas the other is a collaborative effort with the Process Measurements Division to study the destruction of hazardous wastes using supercritical fluids.

The Division has had a good year from the point of view of outside recognition. Dr. J.M.H. Levelt Sengers received a Humboldt Research Award for Senior U.S. Scientists. As a result, she is spending approximately six months in Bochum, Germany, where she is pursuing experimental and theoretical studies of the diffusion of hydrocarbons in supercritical fluids. Dr. J.V. Sengers, of the Thermophysics Division and the University of Maryland, received the 1991 Yeram S. Touloukian Award of the Heat Transfer Division of the American Society of Mechanical Engineers. The Touloukian Award recognizes Dr. Sengers's internationally recognized contributions to the field of thermophysical properties. Finally, Dr. J.F. Ely and Dr. H.J.M. Hanley did an outstanding job of organizing and co-chairing the 11th Symposium on Thermophysical Properties, held in Boulder, Colorado in June, 1991. The Symposium is the premier conference in the world on thermophysical properties. This year, more than 300 scientists and engineers attended from more than 30 countries.

The Technical Reports describe the activities of the Division in more detail.

B. Selected Technical Reports (Thermophysics Division)

1. Eleventh Symposium on Thermophysical Properties

H.J.M. Hanley, J.F. Ely, and Other Staff Members of the Thermophysics Division

The Eleventh Symposium on Thermophysical Properties was held on the campus of the University of Colorado from June 23 to 27, 1991. This symposium, which continued the series started in 1959, was organized by the Thermophysical Properties Committee of the ASME Heat Transfer Division. Two staff members of the Thermophysics Division (H.J.M. Hanley and J.F. Ely) played key roles in organizing the technical program of the conference and served as co-chairmen of the conference. NIST was the major sponsor for the conference.

This symposium, which convenes every three years, represents the premier international conference concerned with the theoretical, experimental, and applied aspects of the thermophysical properties of gases, liquids, and solids. The conference attracted over 300 participants from 30 countries who contributed over 200 papers. On the basis of the level of the papers and on the interaction generated among the participants, the conference was a great success. The papers reflected how sophisticated experimentation and data analysis have become since the symposium began. For example, radiation scattering (light, x-rays, and neutrons) on the experimental side and computer simulation on the theoretical side are now standard tools. Data automation and on-line data analysis are routine and have made possible experiments on microscopic time and length scales.

The keynote address was given by Dr. Henry McGee, Jr., Division Director of the Chemical and Thermal Systems Division of the National Science Foundation, who assessed the position of science in general, and thermophysical properties in particular, in the budget picture. The Eleventh Symposium was also the forum to present the Second Yeram S. Touloukian Award to Professor J.V. Sengers of the Thermophysics Division and the University of Maryland and to Professor T. Makita of Kobe University, Japan for their distinguished contributions to the study of thermophysical properties. Welcoming remarks at the opening session were given by the Deputy Director of NIST.

2. Release of New Version of REFPROP

J.F. Ely, J.S. Gallagher, M.L. Huber, M.O. McLinden, M.R. Moldover, and G. Morrison

REFPROP is a package of user-friendly PC programs that incorporates a database developed in the Thermophysics Division. The package is used by engineers to screen a wide range of environmentally-acceptable refrigerants as possible replacements to currently-used refrigerants. The tables of thermophysical properties produced by REFPROP are used to predict the efficiency and capacity of machinery that will employ alternative refrigerants. Some users have incorporated the source code from REFPROP into proprietary models for specific machines.

During FY91, REFPROP 3.0 was prepared. It has six new features:

1. It includes a comprehensive equation of state for R134a based on the most accurate thermodynamic information available for this leading candidate replacement refrigerant. The user is encouraged to exploit it when dealing with pure R134a. However, the Carnahan-Starling-DeSantis (CSD) formulation remains available for comparative studies.

2. Routines for applying an Extended Corresponding States (ECST) model based on R134a are implemented for all pure fluids on the REFPROP menu. Users have the option of choosing either the new ECST routines or the existing CSD routines.

3. The thermal conductivity and shear viscosity are now predicted for all pure fluids and mixtures on the REFPROP menu.

4. The number of pure components on the menu has been increased by 6 to a total of 26.

5. An explicit rule for predicting mixing parameters from dipole moments is incorporated. The rule is applicable to all but one of the fluids on the menu; see Report #3.

6. The surface tension of pure refrigerants is estimated. The surface tension is used for modeling boiling heat transfer.

95 copies of REFPROP 1.0 and REFPROP 2.0 were sold by the Standard Reference Data Program (SRDP) and approximately 70 copies were distributed by the Air Conditioning and Refrigeration Institute under an agreement with SRDP.

The development of REFPROP is continuing. As new data become available, they will be included in the package. Research is underway to incorporate dipole moments explicitly in a CSD-type equation of state. If this research is successful, fluids such as R32, ammonia, water, and their mixtures can be added to the package. Ideally, REFPROP will include all stable, small molecules that could plausibly be used as working fluids.

3. Prediction of Azeotropy in Refrigerant Mixtures

G. Morrison and M.O. McLinden

Azeotropic mixtures are of particular interest to the air conditioning and refrigeration industries because they can be treated as pure working fluids when machinery is designed, operated, and serviced. In particular, if a portion of an azeotropic mixture leaks from a refrigerator during use or servicing, the composition of the remainder of the charge will be unchanged from that of the initial charge and the lost fluid can be replaced without expensive field measurements. The importance of azeotropes is underscored by the fact that they may be patented.

Phase equilibria data for 24 binary mixtures of halogenated methanes and ethanes were correlated with the dipole moments of the pure components. The correlation was used to estimate the unlike interaction parameters that occur in the 300 binary mixtures of the 25 refrigerants that appear in REFPROP (See Report #2.). The estimated interaction parameters were used to explore the phase behavior of the 300 mixtures, resulting in predictions that 65 of these mixtures have azeotropes at pressures where refrigeration machinery operates. Only 23 of these azeotropes had been reported in extensive compilations of such information. In no case has the correlation failed to predict a known azeotrope, and in no case has it predicted an azeotrope where one is known not to occur.

In effect, this work has shown industry where to look for 42 new "refrigerants." This vastly extends the range of options available to engineers who must re-design thermal machinery in response to the Montreal Protocol, an international agreement that phases out manufacture of the most widely used refrigerants. This project is a textbook example of NIST proposing original solutions to a national problem with industrial, environmental, and energy-conservation aspects.

4. International Activities on CFC Alternatives

M.O. McLinden and W.M. Haynes

The Thermophysics Division initiated and serves as "operating agent" (coordinator) for a project entitled "Thermophysical Properties of the Environmentally Acceptable Refrigerants" under the auspices of the International Energy Agency (IEA). The objectives of this project, known as Annex 18, are (a) to provide a forum for the exchange of information and data and for the coordination of activities on the thermophysical properties of environmentally acceptable refrigerants, and (b) the determination (including experimental measurements and the evaluation and correlation of data) of the thermophysical properties of these fluids leading to the publication of a comprehensive, internationally accepted properties bulletin.

Annex 18 was formally approved by the IEA in early 1990. At present, Austria, Canada, Germany, Japan, Sweden, the United Kingdom, and the United States have officially joined the Annex. In addition to NIST, the United States is represented by Texas A&M University, the University of Idaho, and Cornell University. Formal meetings of the Annex have been held thus far in Japan, Germany, and the United States.

The first task of the Annex was to survey current activities on the measurement and modeling of refrigerant thermophysical properties. Keio University of Japan and the National Engineering Laboratory of the United Kingdom assisted NIST in this effort, which was published as NIST Internal Report 3969. A task on analysis techniques for refrigerant sample purity was also completed by NIST in the fall of 1990 and published as NIST Special Publication 794 and Technical Note 1340. A task to compile experimental thermophysical property data has been initiated. Keio University and Kobe University, Japan have conducted an extensive literature survey of the data available for R134a and R123. NIST has conducted a literature survey, including older data, for the thermodynamic properties of ten alternative refrigerants. Chalmers University, Sweden has begun the task of extending the U.S. search to include additional sources. The focus of effort in the coming year will be an evaluation of experimental data and equations of state for R134a and R123. The University of Idaho and Imperial College will carry out the evaluation, assisted by NIST and Keio University.

The Division has also participated in the second technical reassessment associated with the Montreal Protocol on Substances that Deplete the Ozone Layer. This international treaty, which regulates the production of CFCs and other ozone depleting substances, calls for periodic technical, scientific, and economic reviews of its provisions. M.O. McLinden served on the panel responsible for the "Technical Options Report" on refrigeration and air-conditioning uses of CFCs and acted as lead author for the "Refrigerant Data" section in this report. This review was coordinated by the United Nations Environment Programme and will serve as input for the re-negotiation of the phase-out timetable and other provisions of the Protocol in 1992.

5. Measurements of the Thermophysical Properties of CFC Alternatives

A.S. Aragon, D.R. Defibaugh, D.E. Diller, K.A. Gillis, A.R.H. Goodwin (Guest Scientist), J.B. Howley, A. Laesecke (Guest Scientist), J.W. Magee, C.W. Meyer (836), G. Morrison, M.R. Moldover, V.G. Niesen, C.A. Nieto de Castro (Guest Scientist), S.L. Outcalt, R.A. Perkins, J.A. Sandarusi, J.W. Schmidt, L.J. Van Poolen (Guest Scientist), and L.A. Weber

The Thermophysics Division has been involved in measuring the thermophysical properties of refrigerants since 1982. This early effort was coordinated with the Building Environment Division's program to develop more efficient heat pumps and cooling systems. With the advent of the Montreal Protocol, which restricted the future production of certain fully halogenated chlorofluorocarbon (CFC) refrigerants, the need for environmentally-acceptable substitutes became obvious. In response, and with advice from other government agencies and industry, the Division developed a priority-ordered list of candidate replacements and a strategy for determining their properties. The strategy included developing apparatus for efficiently acquiring data. For the leading candidate replacements, the Division scheduled very accurate, wide-ranging measurements. Less comprehensive measurements, suitable for screening purposes, were scheduled for a second tier of candidates and for "long shots."

Finally, an efficient approach to disseminating the results of the measurements was identified. This entailed correlating the data with the Carnahan-Starling-DeSantis (CSD) equation of state and distributing the results as a user-friendly computer package incorporating the correlations. (See Report #2.)

During the past year, a variety of thermophysical properties measurements were performed on a number of fluids. The properties and fluids studied included

1. Gas-Phase PVT: R22, R32, R124, R125.
2. Liquid-Phase PVT: R11, R22, R32, R123, R124, E245.
3. Coexisting Densities: R22, R32, R124, R125, R134a, R152a.
4. Dipole Moment: R113, R113a, R152, E245.
5. Vapor Pressure: R22, R123, R124, R134a, R141b, R152a, E245.
6. Critical Parameters: R124, E134, E245.
7. Vapor-Phase Speed of Sound: R134a, E134, E245.
8. Viscosity: R123, R124, R134a, R141b.
9. Thermal Conductivity: R124, R125, R142b, R143, E245, E263.

The Division received support for some of these efforts from the Environmental Protection Agency, the Department of Energy, and the U.S. Navy. In FY 1992, the Division plans to perform comprehensive measurements of the thermodynamic and transport properties of R32, R124, and R125, which are three of the most promising but least characterized alternative refrigerants.

6. Release of SUPERTRAPP

M.L. Huber, J.F. Ely, and D.G. Friend

During the past several years, the Division has completed and is continuing to upgrade SUPERTRAPP, which is a user-friendly, interactive, predictive microcomputer program for the calculation of the thermophysical properties of hydrocarbon pure fluids and mixtures. SUPERTRAPP provides property information useful to the engineering community such as density, heat capacity, enthalpy, entropy, speed of sound, Joule-Thomson coefficient, thermal conductivity, and viscosity. In addition, it performs phase equilibrium calculations. It may be used for pure fluids or for mixtures of up to 20 components, and includes a database of 116 fluids. The components in the database cover a variety of hydrocarbons such as n-alkanes up to C_{24}, branched alkanes, alkenes, aromatics, and cycloalkanes. The user also has the option of adding new components to the database. The minimum data required to add a new component are the critical point parameters, the normal boiling point, and the molecular mass.

SUPERTRAPP uses the extended corresponding states method. This very powerful method enables the user to predict thermophysical properties when experimental data are extremely limited or even nonexistent. The Division has used this method in the development of computer packages for air, for mixtures with CO_2, and for halocarbon refrigerants. As the model improves, so do SUPERTRAPP and the other packages based on extended corresponding states.

SUPERTRAPP is available for PC-type microcomputers as an interactive program. A subset of SUPERTRAPP is available as a linkable Fortran library for those users who want the flexibility to implement SUPERTRAPP calculations within their own applications. Future versions of SUPERTRAPP will include a wider variety of phase equilibrium calculations, expanded table generating capability, and inclusion of an improved critical enhancement for thermal conductivity. Additional goals are to develop the capability to make predictions given only the molecular structure, and to improve the "friendliness" of the interactive package. SUPERTRAPP is available through the Standard Reference Data Program of NIST.

7. Completion of Major Project on the Properties of Air

J.W. Magee, J.B. Howley, W.M. Haynes, R.A. Perkins, R.T Jacobsen (University of Idaho), D.E. Diller, J.F. Ely, M.J. Hiza (Contractor), B.A. Younglove, and J.C. Rainwater

Accurate thermodynamic and transport property data for air, especially at low temperatures, are crucial in the design, test, and analysis of the propulsion system to be used in the development of the National Aero-Space Plane (NASP). Thus, a research program has been carried out at NIST to substantially reduce uncertainty levels for the thermodynamic, phase equilibria, and transport properties of air and related mixtures down to the solid line. The major objective of this project was to provide computer codes that could be used for the accurate prediction of the thermophysical properties of air and related mixtures of nitrogen, oxygen, and argon over wide ranges of conditions, but especially at low temperatures.

Comprehensive, state-of-the-art experimental measurements of pressure-volume-temperature (PVT) behavior, sound speeds, heat capacities, liquid-vapor equilibria, viscosities, and thermal conductivities have been carried out for the liquid, vapor, and gas phases of air. These measurements, which concentrated on the low temperature liquid region where liquid neon was needed for refrigeration for temperatures less than 70 K, were made primarily on carefully prepared samples of a standard air mixture with a nominal mole fraction composition of 0.78 N_2 + 0.21 O_2 + 0.01 Ar. Thermal conductivity data were also obtained for two nitrogen + oxygen mixtures with nitrogen mole fractions of 0.25 and 0.5, while vapor-liquid equilibrium (VLE) measurements were made along isotherms as a function of composition for all binary combinations of nitrogen, oxygen, and argon in addition to the ternary mixture.

These experimental data have been used to develop and test a significantly improved equation of state for air, which covers a temperature range of 60 to 873 K at pressures to 70 MPa. This new equation is of standard reference quality and should serve in that capacity for the foreseeable future. Accurate predictive models for the thermophysical properties of mixtures of nitrogen, oxygen, and argon have been developed by carefully integrating the experimental data with the latest theoretical developments in mixture models, such as extended corresponding states. These models have been provided in the form of interactive, user friendly computer codes that can be readily used on microcomputers; mainframe versions of the codes have also been provided to facilitate use with NASP design codes. These computer packages are distributed through the NASP Joint Program Office.

To facilitate rapid development and dissemination for the predictive models and corresponding computer packages, three separate models have been developed: for thermodynamic properties; for viscosity, thermal conductivity, and mixture properties; and for surface tension calculations. As a final product, all of these models are being combined into a single computer package. This final model will be easy to use either in an interactive mode or in conjunction with other computer codes. Although the focus of this project has been directed at the low temperature needs of the NASP program, the wide-range experimental data and models for air may provide large benefits to the chemical process industry in the U.S., for example, in the design and operation of air separation plants.

8. Studies of the Properties of Natural Gas Mixtures

J.W. Magee, T.J. Bruno, W.M. Haynes, B.A. Younglove, J.B. Howley, J.F. Ely, M.L. Huber, J.E. Mayrath, S.L. Outcalt, and D.G. Friend

The Thermophysics Division has been engaged in a comprehensive experimental and theoretical research program for two decades to provide the natural gas industry and the rate payer with the validated property data needed for custody transfer transactions, for energy optimization in gas industry operations, and for the design and control of gas processes. This work has been supported primarily by the Gas Research Institute (GRI).

One major focus of the NIST research program for GRI during the past year has been with an international cooperative research effort to provide a validated set of state-of-the-art (uncertainty of ± 0.05%) PVT data for key natural gas mixtures. This internationally accepted set of PVT reference data, which covers a temperature range from 210 to 360 K at pressures to 35 MPa, will be applied to a wide range of gas measurement applications. Industry applications include both domestic and international gas custody transfer, meter calibration for large volume gas measurement, gas processing measurement, gas storage and reserve estimation, and general thermodynamic calculations in gas engineering. These data will also be used to evaluate, develop, and improve equations of state for gas mixtures. The other participants in this round-robin series of PVT measurements are Texas A&M University, van der Waals Laboratory, and Ruhrgas. This project represents a major cooperative effort between U.S. and European interests in the natural gas industry.

Five gas mixtures of commercial interest were selected for study in this project. Since it is extremely important that the mixture compositions be known to high accuracy, eleven cylinders of gas samples were prepared with the utmost care at NIST for the targeted compositions and distributed to each of the participants for measurement. Measurements at NIST have been carried out using an isochoric gas expansion apparatus over a temperature range of 225 to 350 K at pressures to 35 MPa. Approximately ten isochores have been measured for each mixture at densities from 1 to 16 mol/dm^3.

It is expected that this set of high accuracy data will play an instrumental role in custody transfer applications in the natural gas industry for many years; new models can be tested and validated with this set of data for key natural gas mixtures representative of a wide range of compositions bought and sold on the world market. The temperature and pressure ranges cover the major current and projected custody transfer regions for the natural gas industry. After the evaluation of the data is completed at the van der Waals Laboratory, the results of this project will be published as a NIST Monograph.

During the past year a NIST Monograph has been prepared that details the results of sound speed studies of natural gas mixtures. Its completion was delayed until the revised AGA-8 model (industry standard for computations of compressibility factors for natural gas mixtures for gas volume calculations and field testing of meters) was available so that the monograph would include comparisons of the new model with the NIST sound speed data which have been used as input in the development of the model. The monograph includes a description of the experimental techniques, procedures, and uncertainties; tables of the experimental results; a description of the predictive model for sound speed and density developed at NIST; and comparisons with the revised AGA-8 and NIST models. These experimental data cover temperatures from 250 to 350 K at pressures to 10 MPa for thirteen binary mixtures and four multicomponent mixtures of natural gas components. Both the NIST and AGA models are generally accurate to within ± 0.1% for sound speeds (and densities) in the temperature and pressure range where most custody transfers take place. Not only are the sound speed results useful for sonic nozzle metering applications, but they have also proved valuable in the development of a correlation for supercompressibility factors adopted as an industry standard for custody transfer in determining the volumetric flow rates of orifice and turbine meters.

Because of the increasing importance of the influence of trace constituents on the accurate modeling of natural gas properties, the Thermophysics Division has undertaken an experimental program of property measurement of some of these constituents. These trace constituents include inorganics such as water, and organics such as halogenated hydrocarbons and waxes. The measurement program is currently focused on vapor pressures and solubilities of trace constituents such as the halogenated hydrocarbons. The vapor pressures are especially important for modeling, since they provide acentric factors (needed for many cubic and higher order equations of state) and, therefore, a route to predicted critical properties. It is expected that this program will provide the natural gas indtry with the necessary data to understand and model the transport of halogenated hydrocarbons in natural gas lines.

9. Development of New Measurement Technologies for Thermophysical Properties

R.F. Chang, N.V. Frederick (Contractor), W.M. Haynes, R.F. Kayser, J.W. Magee, M.O. McLinden, M.R. Moldover, G. Morrison, R.A. Perkins, and L.A. Weber

The development of instrumentation to measure thermophysical properties and to extend the measurement capabilities currently available requires the highest in scientific and engineering skill. By the early 1980s, this was a research field in which the U.S. had declined significantly relative to the rest of the world. To address this problem, the Thermophysics Division and the Department of Energy initiated a major long-term program to develop new apparatus for measuring thermophysical properties . As part of this program, the Division recently began a new five-year effort to develop apparatus applicable to complex fluids and fluid mixtures important to the energy, chemical, and energy-related industries. In addition to extending the state-of-the-art, these new apparatus will make it possible to study highly polar, electrically conducting, and reactive fluids under conditions that have been previously inaccessible.

The instruments under development include: (1) Thermal Conductivity Apparatus, which will allow studies of the thermal conductivity and thermal diffusivity of electrically conducting fluids such as aqueous solutions and highly polar liquids such as refrigerants, (2) Vibrating Wire Viscometer, which will make it possible to obtain highly accurate data at high temperatures far more routinely than is the case at present, (3) Dual-Sinker Densimeter, which will yield standard-reference-quality pressure-volume-temperature data over a wide range with a single apparatus, (4) High-Temperature Vibrating Tube Densimeter, which will extend the range and applications of this technique to much higher temperatures than are accessible at present, (5) Dynamic Phase Equilibria Apparatus, which will be ideal for characterizing fluids in the important temperature range from -50 to +150 °C, (6) Apparatus for Dilute Solutions, which will be suitable for measuring infinite dilution activity coefficients, (7) Total-Enthalpy Flow Calorimeter, which will allow accurate characterizations of fluids that are reactive or chemically unstable at high temperatures, and (8) Dielectric Constant Apparatus, which will make it possible to obtain molecular dipole moments and polarizabilities, which are needed to develop reliable models for the thermophysical properties of polar fluids and mixtures that contain highly polar components.

The Dual-Sinker Densimeter and High-Temperature Vibrating Tube Densimeter illustrate the quality of the instruments under development. In the Dual-Sinker Densimeter, two sinkers of identical mass, surface area, and surface material, but very different volumes, will be weighed separately with an analytical balance while immersed in a fluid of unknown density. The difference in buoyancy forces on the two sinkers will yield ρ, the fluid density, via $\rho = \Delta F/\Delta V$, where ΔF is the difference in the apparent sinker weights and ΔV is the difference in sinker volumes. The sinkers will be suspended from the balance via a magnetic suspension coupling that isolates the balance from the high-pressure measuring cell. The main advantage of the dual-sinker method is that surface tension effects on the suspension wire, adsorption onto the surface of the sinkers, and other effects that reduce the accuracy of most buoyancy techniques cancel. A further advantage is that the difference in buoyancy forces yields the fluid density directly, without the need for calibration fluids. Accuracies of better than 0.01%

over wide ranges of temperature, pressure, and density, will be routinely achieved. At this point, the design, fabrication, and testing of the various elements of the dual-sinker densimeter have proceeded in parallel. The analytical balance and mock-ups of the magnetic coupling and sinker changing mechanism have been tested successfully, and the design of the sinkers and the pressure vessel have been finalized and fabrication begun. The final elements of the system, including the vacuum system, filling manifold, and instrumentation, are under development.

In the case of the High-Temperature Vibrating Tube Densimeter, a prototype has been designed and fabricated that will have a precision of 10^{-4} g/cm^3 at temperatures to 400 °C. In common with commercially available vibrating tube densimeters, the sample is confined to the interior of a continuous, stainless-steel tube. The tube is caused to oscillate in a bending mode and the density of the sample is determined by the change that it causes in the resonance frequency of the mode under study. However, in contrast to the commercial densimeters, the prototype does not use cements, glues, or polymer insulations of any kind. The current design also has the following unique features: (1) the use of a current passing through the tube to cause the tube to oscillate in the field of a permanent magnet, (2) the use of the voltage induced in the tube by its oscillation in the field to detect the oscillation, (3) the optional use of higher frequency modes of oscillation than the lowest bending mode of the tube, and (4) the optional use of a bridge arrangement in the detection circuitry that incorporates a non-oscillating portion of the tube to compensate for the temperature dependence of the electrical impedance of the tube. Each of these features has been demonstrated with the prototype. During the next year, the room-temperature stability of the densimeter will be tested and an oven will be designed and fabricated so that tests at higher temperatures can begin.

10. Neutron Scattering Studies of the Structure of Fluids

H.J.M. Hanley and G.C. Straty

It is well known that the behavior, and hence the variation of a fluid property with experimental conditions, is dominated by the microstructure or particle positional order of the fluid. The microstructure is best investigated by the combination of radiation experiments on real liquids, and computer simulations on models. The common radiation probes are x-rays, light, and neutrons, but neutrons have several advantages principally because the scattering is at the level of the nucleus. Scattering from the nucleus means that isotopic substitution is a tool. Selective substitution of D for H in a molecule, for example, is an effective trick to monitor only those parts of a molecule that one wants to see. Scattering from the nucleus also permits the technique of contrast matching, wherein portions of a fluid (i.e., a given species or parts of a given molecule) can be made invisible to neutrons so that the scattering pattern results only from the portion that one wishes to observe.

Work in the past year involved becoming familiar with the new 30 m SANS (small angle neutron scattering) instrument at the NIST reactor facility. The shearing cell built by us for the facility was automated. The shearing cell is now fully operational and available for users; in fact, experiments have been carried out with staff of the University of Illinois and

Oklahoma State, and will be conducted shortly with scientists from Exxon and the University of Bristol.

Our investigations of the structure of colloidal suspensions and suspension mixtures continued. Scattering experiments were carried out at NIST and at the low-angle neutron scattering facility of Los Alamos. Unfortunately, some experiments had to be cancelled because of the breakdown at the Institute Laue Langevin (ILL) facility in Grenoble.

The Division has essentially completed the experimental side to a long range study of partial structure factors of the components in a suspension. The partial structure factors were estimated by contrast matching: namely, the partial scattered intensities in a given mixture were measured by selecting a solvent with the scattering length density that matches one of the components. The results are novel and will contribute to a better understanding of the behavior of mixtures in general. Experiments were performed for the system under shear. The data are inputs to a parallel theoretical investigation on the theory of mixtures, a task which is ongoing.

The experimental studies of the shear-induced melting phenomenon and of whether or not a solid-like structure can be introduced into a liquid by the action of a shear continued. The data are being analyzed. A theoretical study of the melting process is underway. The results are of interest to colloidal chemists, but have a wider impact in that they can be used as input into statistical mechanical and thermodynamic theories for a system far from equilibrium. Furthermore, the experiments were performed in conjunction with experiments on the rheological behavior of dense suspensions, leading to a connection between transport properties and structure.

Experiments were started on intermolecular structure and chemical reactions using the gelling of silica as a model system. These experiments will be expanded in the near future.

11. Advances in the Theory and Modeling of Thermophysical Properties

D.G. Friend, J.C. Rainwater, M.L. Huber, J.R. Fox, H.J.M. Hanley, J.F. Ely, J.J. Lynch (University of Colorado), C.A. Nieto de Castro (Guest Scientist), R.A. Perkins, and R.L. Rowley (Faculty Appointment)

A primary focus of the Division's theoretical effort is to develop and apply microscopic theories of fluids to the prediction and correlation of both equilibrium and nonequilibrium behavior of pure fluids and mixtures. The modeling efforts often encompass broad ranges of state variables and incorporate theoretical advances as appropriate. Correlations of fluid properties and predictive models are distributed through the Standard Reference Data Program in the form of computer packages such as MIPROPS, DDMIX, REFPROP, and SUPERTRAPP.

During the past year, our descriptions of phase equilibria at high pressures were extended to include higher-order terms in the standard renormalization group calculations. These extended scaling or Wegner corrections were tested on data for binary systems containing

CO_2 and butane. The vapor-liquid coexistence boundary for systems exhibiting double retrograde condensation were also described and our models were extended to account for the behavior of systems with critical azeotropy. Our recently derived asymptotic expressions for dilute mixtures may lead to simpler predictive models for vapor-liquid equilibrium. Investigations of mixture generalizations of the Clausius-Clapeyron relationship are underway to calculate coexisting enthalpies and entropies in the near-critical region from the scaled equations.

In the area of transport properties, the Division recently developed a powerful new predictive method based on corresponding states with mass shape factors. It also proved possible to combine our theoretical knowledge in three regions of the state variables to correlate the thermal conductivity of argon with great accuracy. This involved our understanding of the dilute gas behavior, our theory of the moderately dense gas, and our understanding of the critical region enhancement based on mode coupling theories. The NIST theory for the moderately dense gas has now been widely adopted and was used to develop standard reference correlations for a variety of simple systems. Our calculation of the critical region enhancement is being used for numerous systems, including methane, ethane, nitrogen, and R134a, and is also being extended to binary mixtures. Structural contributions to the dynamic behavior of fluids were studied through nonequilibrium molecular dynamics simulations of molecules undergoing shear flow. The site-site model for n-butane and i-butane provided simulational results in substantial accord with experimental viscosity data.

Finally, the development of highly accurate theoretically based correlations of the thermophysical properties of pure fluids has continued. Work was completed on ethane and helium, and projects on R134a, other refrigerants, heptane, hexane, and xenon are underway. Our recently developed pure fluid equations of state for the lower alkanes - which provide an excellent description of the behavior of these fluids in the general critical region - were used successfully to calculate mixture properties. This study compared purely classical calculations of the dew-bubble coexistence boundary and single-phase thermophysical properties with experimental data for the methane-ethane system.

12. Computer-Simulation of Water with Ab Initio Intermolecular Potentials

R.D. Mountain and W.J. Stevens (831)

Computer simulation of the dynamics of molecules in liquids makes it possible to obtain reliable theoretical estimates of thermodynamic and transport properties provided the proper force laws are used. Since water is part of many interesting systems, it is important to understand the physics of the water-water interaction in the liquid state before undertaking extensive simulations of systems containing water.

The Division is attempting to identify the important physics of the water-water intermolecular potential and force law. Current efforts are using the results of ab initio water-dimer energy calculations to provide a well-characterized force law. This force law is used in molecular dynamics simulations of the molecular motions in the liquid state to obtain the site-site pair distribution functions, which are quantities known from scattering experiments. Comparisons of the computed functions with the experimental results show how well the dimer-based results carry over to the liquid environment. Our initial results indicate that polarizability effects are a promising way of including many-body interactions in terms of dimer properties and that the polarization sites of a molecule should reflect the geometry of the molecule. A hope is that the many-body interactions can be adequately represented in terms of the polarization induced by the permanent dipole moments of the molecules.

A new parameterization of the dimer energy surface will be generated to incorporate the results of the initial study. This model will be tested extensively and the results will be published. Once the necessary physics in the water-water interaction has been identified, other cases, such as water-hydrocarbon and water-ion systems, will be studied.

13. International Activities on Water and Steam

J.M.H. Levelt Sengers, J.V. Sengers, and J.S. Gallagher

The International Association for the Properties of Water and Steam (IAPWS) is planning to produce a new scientific formulation to replace the well-known NBS/NRC Steam Tables of 1984. The target date for adoption is the 1994 International Conference on the Properties of Water and Steam, which will be held in the United States. IAPWS is also considering the development of a new industrial formulation to replace the 1967 formulation (IFC67), which is the basis for the design and evaluation of steam boilers and turbines worldwide. The new industrial code must be at least three times faster than the IFC67 code, but no less accurate. Colleagues in Germany, Canada, Japan, the U.S.S.R., and the U.K., among others, have stated their plans to participate in the development of the new formulations.

From the perspective of IAPWS, as well as that of NIST and data users in the U.S., NIST involvement in the new scientific and industrial formulations is highly desirable. The NBS/NRC Steam Tables have found wide use in chemical engineering, chemistry, geology, and in commercially-available data bases and software. Moreover, environmental problems and concerns have created a strong new impetus for work on the quality of water and water effluents, and on the use of water at high temperatures and pressures to process hazardous wastes.

During the past year, the Division and its collaborators completed a computerized data base containing approximately 16,000 evaluated data points on the properties of water and steam. The data base will form the basis for the new IAPWS scientific formulation. The collection includes a review and assessment of the accuracy of all experimental data obtained during the past century and considered reliable. Properties include vapor pressure, heat of evaporation, density, enthalpy, heat capacities, sound velocity, and Joule-Thomson coefficients; the data cover stable and metastable one-phase states as well as two-phase states. The data are in a common set of units, including the new ITS-90 temperature scale.

For the next several years, NIST will continue to participate in the development of the new scientific and industrial formulations. With regard to the former, the Division plans to develop crossover equations for the critical regions of light and heavy water, to compare the predictions of the new formulation with experimental data for supercooled water, to test the new formulation, and to reformulate the transport properties; the Division may also reformulate the dielectric constant and Debye-Huckel coefficients. With regard to the industrial formulation, the Division will be involved in efforts to develop and test faster computer algorithms.

Members of the Division occupy prominent positions within IAPWS and the American Society of Mechanical Engineers (ASME). J.H.M. Levelt Sengers is simultaneously the President of IAPWS and the U.S. National Delegate to IAPWS from the ASME Research Subcommittee on the Properties of Water and Steam. J.S. Gallagher is Secretary of the ASME Research Committee on the Properties of Water and Steam.

14. New Volume on Supercritical Fluid Technology

T.J. Bruno, J.F. Ely, J.M.H. Levelt Sengers, J.C. Rainwater, and J.W. Magee

Two members of the Thermophysics Division, T.J. Bruno and J.F. Ely, are editors of a definitive volume (Supercritical Fluid Technology - Reviews in Modern Theory and Applications, CRC Press, 1991) that reviews the theory and application of supercritical fluids in industrial scale separations. During the past five years there has been renewed interest in supercritical fluid extraction methods for industrial applications. Following some initial disappointments, it is now clear that supercritical fluid technology has many industrial applications, but the systems must be chosen carefully. The best candidates are high cost, low volume commodities that require the use of nontoxic solvents in processing. These materials include pharmaceuticals, flavors, foods, and essential oils. In addition, there are potential applications in environmental cleanup and polymer processing.

The 600 page book contains a series of reviews, provided in 16 chapters. The volume has been divided into experimental and theoretical sections. Major contributions have been made in both sections by members of the Division. A detailed treatment of the thermodynamic behavior of dilute mixtures and solutions near the solvent's critical point has been provided by J.M.H. Levelt Sengers. J.C. Rainwater has contributed a comprehensive review of vapor-liquid equilibria of binary mixtures and their correlation with the Leung-Griffiths model. On the experimental side, T.J. Bruno has given a summary of thermophysical property data important to supercritical fluid extraction process design along with general descriptions of experimental apparatus that can be used to acquire these data. J.W. Magee has presented a survey of evaluated data for both the thermodynamic and transport properties of CO_2 and CO_2-rich mixtures. A summary of the patent literature of supercritical fluid technology for the 1980s has been compiled by T.J. Bruno. Other major topics include chapters on molecular analysis of phase equilibria, Kirkwood-Buff fluctuation theory of mixtures, molecular simulation, transport properties, mass transfer, microemulsions, chemical reactions, engineering parameters, and applications in biotechnology and environmental technology.

15. Properties of Solids and Liquids at Very High Temperatures

A. Cezairliyan, J.L McClure (Contractor), A.P. Miiller, and R.A. MacDonald

In this area, the Division develops new techniques and performs measurements of selected thermophysical properties of electrically-conducting materials (in solid and liquid phases) at high temperatures (1500-5000 K). This requires subsecond-duration (millisecond and microsecond-resolution) pulse heating techniques to make measurements above the limits of conventional steady-state methods. The research output serves high-temperature technologies related to spacecraft, nuclear reactors, engines, weaponry, effects of powerful lasers, materials processing, reference materials, reference data, and validation of theoretical models in related areas.

During the past year, development of a new method for thermal conductivity measurements based on resistive self-heating of the specimen and measurements of the transient temperature distributions in the specimen has started. The necessary analytical solution of the transient heat transfer equation was developed, and a recently completed spatial scanning pyrometer was tested. Preliminary measurements on molybdenum indicated the feasibility of the technique for accurate thermal conductivity measurements at temperatures above the limits of conventional methods.

The behavior of the normal spectral emissivity of molybdenum at its melting point was investigated. The results showed that the emissivity decreases significantly as the wavelength increases, which is in contradiction with the constant emissivity found by a major European laboratory. This finding has very significant implications, as the emissivities of metals at their melting point are being considered as reference values.

Tungsten has the highest melting point (~3700 K) among the metals, and as a result it has been difficult and often impossible to measure its properties near its melting point. The microsecond system was used to accurately measure the heat of fusion of tungsten.

Future plans include (1) the development of new techniques for measuring other properties, such as speed of sound, mechanical properties, viscosity, etc., (2) the development of techniques to perform measurements under combined high-temperature high-pressure conditions, (3)measure-ment of properties of advanced materials (metallic alloys and graphitic composites), and (4) theoretical studies of the behavior of materials far removed from thermodynamic equilibrium.

16. Gas and Mode-of-Operation Effects in Gas-Operated Piston Gages

R.G. Driver, C.D. Ehrlich, J.C. Houck (Contractor), J.L. Kelley, B.A. Ratnam, J.W. Schmidt, B.E. Welch (Contractor)

Gas-operated deadweight piston gages are the instrument of choice in the atmospheric pressure range for most applications where high accuracy, low cost, ease of use, and transportability are important considerations in the transfer of the unit of pressure between laboratories, or from the laboratory to the field. The increasing use of 'accuracy ratios' as regulatory guidelines in propagating uncertainties in effective area has led to requests for total uncertainties at the national standards level of well under 50 parts per million (ppm). These levels of uncertainty tax the performance of some of the best available instruments. In particular, the effective areas of these instruments depend on the gas being used, and on whether or not the gage is operating in the absolute mode (essentially vacuum above the piston) or the gage mode (atmospheric pressure above the piston), at the tens of parts per million level. Historically, such effects were not anticipated to be so large, and are still typically ignored by many.

To investigate these gas and mode-of-operation effects, the Division is developing two new apparatus: the Three-Piston-Gage Apparatus (TPGA), which utilizes two piston gages to carefully characterize a third, and the Dynamic-Piston-Gage Apparatus (DPGA), which probes the decay of small amplitude oscillations of the piston to understand the forces acting in the annular region between the piston and the cylinder. Initial work with the TPGA has included the successful 'floating' of all three pistons simultaneously, and an investigation of the effects of gas and mode of operation on the rotational decay rate of a freely rotating piston. The DPGA has been used to measure the natural frequency and quality factor of an oscillating piston at different applied pressures and for different gases.

The rotational decay rates of the freely rotating piston vary significantly for different gases and modes of operation. A model has been developed to describe the torque exerted on the piston by the gas in the annular region between the piston and the cylinder. The model incorporates elements of both viscous and molecular flow theory, and it does a credible job of predicting the observed functional dependencies. A publication describing this work is in progress. The extension of the model to describe changes in the effective area, which are much smaller, will await the full use of the TPGA with all three pistons over a variety of operating conditions. Studies underway with the DPGA will investigate whether the observed damping of the piston is due to viscous forces originating in the annulus, or some other source.

17. New Primary Standard for Transition Range Pressures

R.W. Hyland, J.P. Looney, and D.F. Martin

Many important industrial processes and research projects - thin film sputtering, freeze drying, superalloy processing, and cross section measurements, to name a few - operate in the Transition Pressure range, the range where gas dynamics are in transition from domination by molecule-molecule collisions, to domination by molecule-wall collisions. Typically this occurs in the pressure range between 0.1 and 10 Pa (10^{-3} and 10^{-1} Torr). Unfortunately, the changing gas dynamics affect the performance of vacuum gages, causing significant nonlinearities and complicating the calibration of these gages. Accurate measurements in this range are further complicated by a gap between our low-pressure and high-vacuum standards, and the corresponding calibration services. This prompted the development of a new Transition Range Pressure Standard, designed to operate over the range 10^{-4} to 10^{2} Pa (10^{-6} to

1 Torr) to allow the full-scale calibration of spinning rotor gages and low-range capacitance diaphragm gages.

For use in calibration services, the new standard must be capable of rapid and flexible operation, which can best be achieved with the orifice-flow technique used in our high-vacuum standards. At higher pressures this requires an orifice or conductance with small characteristic dimensions; therefore, the new standard includes a nominal 1 cm diameter orifice for use at low pressures, and an array of 4900 laser-drilled holes, 3-5 micrometers in diameter, for use at higher pressures. Our expectation is that the latter will generate pressures linearly over most of the range of the standard. To check the linearity of the array, the standard is designed to operate in a volume-expansion mode, which is slow, but independent of gas dynamics.

Operation of the standard this past year has been quite satisfactory at low pressures using the conventional orifice, but disappointing at higher pressures where the array must be used. The small conductance of the array (1.5×10^{-3} l/s) results in a system time constant of several hours, and pressure equilibrium is very difficult to achieve. Further, the necessity to maintain the accuracy of capacitance diaphragm gages needed for the volume expansion measurements, using a standard located elsewhere in the laboratory, has proven to be very time consuming.

The transfer standard calibration problem has been addressed by refurbishing an early, 100 Torr range version of the Ultrasonic Interferometer Manometer, and incorporating it into the new standard. This has improved not only the efficiency and accuracy of the volume-expansion measurements, but it should also allow a more efficient calibration service for low-range capacitance diaphragm gages. The time constant problem requires a conductance at least two orders of magnitude larger than that of the present array. At $1/hole this is prohibitive using laser drilling. However, recent experiments elsewhere in the Group (see Report #18) have found that microchannel plates have a conductance of 0.1 l/s, which will be ideal for the Transition Range Standard. At this writing a microchannel array is being prepared to replace the laser-drilled array in the Transition Range Standard. Characterization of this new conductance will start as soon as it is installed, and the entire system should be operational in the coming year.

18. Absolute Standard for Low-Density Water Vapor

C.R. Tilford and S.A. Tison

The environment in vacuum processing chambers is often dominated by undesirable residual gases. The most common, and often most undesirable, is water; very small amounts of water will cause undesirable changes in semiconductor characteristics, spoil the adherence of thin films, and cause later failures in electrical interconnects. Water is also a major problem in space environments; several satellite optical systems have failed because of the condensation of outgassed water onto optics and detectors, and condensed water has caused destructive discharges in high-density electronic packages. However, in spite of the obvious importance of accurately monitoring the water generated in vacuum systems, vacuum standards laboratories have shied away from this problem; no standards exist for low-density water, and very little is known about the effects of water on vacuum gages. The Division is trying to address this problem by developing a primary standard for water vapor over the range 10^{-5} - 10^{-2} Pa (10^{-7} - 10^{-4} Torr).

The well-proven orifice-flow design is the best technical choice for the new standard, and a Knudsen-effusion source is being used to generate known flows of water vapor. This source incorporates two molecular conductances: an array of 100 laser-drilled holes, each about 5 micrometers in diameter, and a microchannel plate, a 1 mm thick glass disk with 2.4 million cylindrical holes 5 micrometers in diameter. Within the range where these conductances are molecular, i.e., the range where conductance is constant, or the flow is proportional to the upstream pressure, the conductances can be determined for a gas such as nitrogen, and scaled by the square root of molecular weights to determine the water conductance.

Measurements to date have found the nitrogen conductance of the laser-drilled array to be molecular to within 1% up to 1000 Pa, and the ratio of the nitrogen and helium conductances to scale with molecular weights to better than 1%. The conductances of the microchannel plate have proven to be significantly larger than expected, basically too large for this application, and the nitrogen and helium conductances have failed to scale by as much as 5%, indicating the possibility of significant specular scattering for helium.

Preliminary calibrations of ionization gages, spinning rotor gages, and a partial pressure (residual gas) analyzer have been conducted between 10^{-4} and 5×10^{-3} Pa using the laser-drilled array. Several hours are required to obtain an equilibrium pressure indication from the gages, a significant but not unexpected limitation that is probably due to surface adsorption in the calibration chamber and/or chemical and surface reactions in the gages. Once equilibrium is achieved, the indicated pressures are surprisingly stable and reproducible. However, the water pumping speed of the common Bayard-Alpert ionization gage appears to be about two orders of magnitude larger than for other common gases, and the accommodation coefficients for the spinning rotor gages are not fully understood.

Current plans are to extend the range of this system by replacing the microchannel plate with a larger laser-drilled array currently used in the Transition Range Standard (see Report #17), and to continue the gage performance experiments. It is anticipated that this system can serve as the basis for a new calibration service.

19. Optical Measurements of Low-Density Gases

J.P. Looney

Limiting factors for many vacuum measurements are the interactions between the gas to be measured and the gages. This is particularly acute for reactive gases, such as oxygen, carbon monoxide, water, and hydrogen. These gases react with the hot filaments and/or high voltage discharge electrodes found in most high vacuum and all ultra high vacuum gages. These reactions can cause significant local perturbations in both the density and composition of the gas.

Surface adsorption at the vacuum chamber walls and on the surfaces of gage components can also perturb the local density, and cause long time responses in gages and vacuum standards. To investigate the magnitudes of these effects for different gases and gages, measurement techniques are needed that measure specific vapor-phase species directly with minimal perturbations.

Optical measurement techniques show the greatest promise to meet these requirements. A number of different techniques have been developed for diagnostic measurements at higher pressures. Some of these techniques are also capable of making spatially resolved measurements, a desirable factor for some experiments. Preliminary work has been undertaken to determine if these techniques can be refined to make quantitative measurements with low-density gases.

In conjunction with the Electron and Optical Physics Division, Resonance Enhanced Multiphoton Ionization (REMPI) measurements, using a time-of-flight mass spectrometer as a detector, have been made for several different gases, including xenon, oxygen, and nitrogen. Xenon, which is relatively easy to ionize, was used to setup and verify the performance of the apparatus. Even for xenon, considerable care must be taken with beam power and focusing geometry. Initial nitrogen measurements have demonstrated linearity of the ion signal as a function of pressure to within 20% down to 10^{-5} Pa (10^{-7} Torr). Very similar results were obtained with oxygen. The oxygen experiments did indicate, as had been postulated before, that the signal from the common Bayard-Alpert ionization gage is limited by electron-stimulated-desorption of oxygen from the gage structure.

As noted in Report #18, water vapor measurements are important, but difficult, and our prototype water standard has a long time constant (hours) associated with surface adsorption/desorption. A promising approach to measure vapor-phase water directly and quickly is infrared absorption. However, absorption measurements are difference measurements, and the low-density limit of such measurements is determined by uncertainties in the baseline, or intensity of the zero-density transmitted beam. This problem has been evaluated using methane as a surrogate for water, in collaboration with the Molecular Physics Division. These experiments show that baseline uncertainties are the limiting factor, but by averaging over several absorption lines, absorption values were obtained down to 10^{-3} Pa (10^{-5} Torr) that were linear with pressure to within 2%. It should be possible to make measurements with water at least one decade lower.

20. Developments in Vacuum Instrumentation

A.R. Filippelli, F.G. Long, J.P. Looney, and C.R. Tilford

The development of measurement standards and calibration services is of little practical use unless stable and predictable transfer standards are available. Since vacuum measurements are relatively new and evolving, knowledge of instrument performance is limited. Therefore, as the NIST vacuum standards have evolved, there has been a parallel effort to characterize, and in some cases to improve, vacuum instrumentation.

Spinning Rotor Gages (SRGs): The SRG is a molecular drag vacuum gage that became commercially available eight years ago and has found increasing use as a transfer standard. One of the limitations of this gage has been the inflexibility of the commercial control unit, particularly its data analysis algorithm. During the past year, a prototype SRG control unit has been designed and assembled that uses a personal computer to execute either one of two different data analysis algorithms. One of the algorithms has worked quite well; random errors are a factor of three or more less than those obtained with the commercial units. The second approach has yet to work as well. The Group plans to refine the design of these prototypes and then to fabricate additional units for its routine use. Details will be published when development is complete.

Cold-Cathode Ionization Gages: The recent introduction of two new commercial cold cathode gages has prompted a study of them. The linearity of the output has been considerably improved over previous models, and the stability is better than that generally reputed to cold-cathode gages. At lower pressures, combined nonlinearities, hysteresis, and changes with time cause the output to vary by ±10% over 6 months to a year. Above 10^{-2} Pa, where these gages are often used, the sensitivity can change by a factor of two or more, depending on the gas. In short, these gages are still not as linear and reproducible as hot-cathode gages, and they have a significantly higher pumping speed. They may be used advantageously in applications where a hot filament cannot be tolerated, or the gage may be exposed to pressures above 0.1 Pa.

Partial Pressure Analyzers (PPAs): The increasing importance of partial pressure measurements in industrial vacuum processing, and a corresponding increase in requests for PPA calibrations, prompted a study of commercial PPAs, the results of which were published two years ago. This study found unexpected behavior in several instruments that could cause errors as large as two orders of magnitude. Research on several of the issues raised by the earlier study have continued, in particular, the cause of shifts in PPA sensitivities for all gases after brief exposure to active gases (such as oxygen or carbon monoxide), the effects of different operating parameters, and the relative importance of design differences and unit-to-unit differences in determining performance variations. A number of new results have been obtained and will be published in the coming year.

21. Improved Leak-Rate Standards

D.F. Martin and S.A. Tison

Leak-rate measurements are an important quality control procedure for many manufactured items. Since the initial development of NIST helium leak-rate standards and calibration services, there has been an increasing demand for calibrations and numerous requests to expand our capabilities, both by extending the range, and developing capabilities for other gases. The demand for other gases has been particularly strong for freons, which are used for general-purpose leak detection, and are of particular interest to the refrigeration industry, which is facing new and stringent allowable leak standards. During the past year, the Division has significantly extended the range of the primary standard, improved the efficiency of the calibration service, and laid the groundwork to develop capabilities for other gases.

The low-range flowmeters that are an essential part of the primary leak-rate standard have a lower operating limit of 10^{-12} mol/s, which had set a corresponding limit for the operation of the standard and the calibration service. Given certain assumptions, it is possible to extend the lower limit of the primary standard to 10^{-14} mol/s using a flow division technique. These assumptions have some theoretical justification, but no experimental verification. During the past year, an experiment has been completed in which the standard, operating in the flow-division mode, was used to measure the leak rate of several variable pressure diffusion leaks. The measured leak rates were linear with concentration to within 1%, in good agreement with the predictions of diffusion theory. This validates the flow-division operation of the primary standard and allows us to extend the range of our calibration service. Several low-range leaks have already been calibrated.

To cope with the growing calibration work load, a new leak calibration system has been designed and fabricated. This system is automated, allows the concurrent calibration of multiple leaks, and has the capability to operate with a variety gases. Two of these systems have also been built for outside laboratories. Two of the three systems are now complete and operating and a third is near completion.

There are no obvious major technical barriers to the extension of our leak-rate capabilities to other non-reactive gases. However, the well-understood diffusion leak that is used as a transfer standard for helium cannot be used with other gases. Unfortunately, there is little reliable data on the stability of other types of transfer leaks, and significant staff time will be required to evaluate transfer leak characteristics, and to evaluate the performance of the calibration systems. Experiments have been carried out with several types of leaks that can be used with other gases, but much more remains to be done, and progress is limited by other demands for the time of available staff.

C. Outputs and Interactions (Thermophysics Division)

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Sato, H., Watanabe, K., Gallagher, J.S., Sengers, J.M.H. Levelt, Hill, P., Straub, J., and Wagner, W., "16 000 Evaluated Experimental Thermodynamic Property Data for Water and Steam," J. Phys. Chem. Ref. Data (in press).

Schmidt, J.W., "Near-Critical Fluid Interfaces - A Comparison of Theory and Experiment," Physica A 172, 40-52 (1991).

Sengers, J.M.H. Levelt, "Solubility Near the Solvent's Critical Point," J. Supercritical Fluids (in press).

Straty, G.C., Hanley, H.J.M, and Glinka, C.J., "Shearing Apparatus for Neutron Scattering Studies. Preliminary Results from Colloidal Suspensions," J. Stat. Phys. 62, 1015-1023 (1991).

Straty, G.C., Pieper, J., and Hanley, H.J.M., "Contrast Matched Studies of a Sheared Binary Colloidal Suspension," Mol. Phys. 72, 241-246 (1991).

Tang, S., Jin, G.X., and Sengers, J.V., "Thermodynamic Properties of 1,1,1,2-Tetrafluoroethane (R134a) in the Critical Region," Int. J. Thermophysics, 12, 515-540 (1991).

Tang, S. and Sengers, J.V., "Thermodynamic Behavior of Fluids in the Supercritical Region," J. Supercritical Fluids (in press).

Van Poolen, L.J., Niesen, V.G., and Rainwater, J.C., "An Experimental Method for Obtaining Critical Densities for Binary Mixtures: Application to Ethane + n-Butane," Fluid Phase Equilibria (in press).

Weber, L.A., "PVT and Thermodynamic Properties of Gaseous R141b," Proceedings of the XVIIIth International Congress of Refrigeration, Montreal, Canada, August 10-17, 1991.

Yang, J.X., Gould, H., Klein, W., and Mountain, R.D., "Molecular Dynamics Investigation of Deeply Quenched Liquids," J. Chem. Phys. 93, 711-723, (1990).

Younglove, B.A. and Frederick, N.V., "Sound Speed Measurements on Mixtures of Natural Gas Components Using a Cylindrical Resonator," Int. J. Thermophysics 11, 897-910 (1990).

2. Talks

Berg, R.F., Designing a Small Viscometer, Thermophysics Division Seminar, NIST, Gaithersburg, MD, April, 1, 1991.

Berg, R.F., Viscosity Near the Liquid-Liquid Point of a Polymer Solution, American Physical Society Meeting, Washington, DC, April 24, 1991.

Bruno, T.J., Process Analytical Chemistry Applied to a New Separator/Solvator for Supercritical Fluid Extraction, International Forum on Process Analytical Chemistry, Houston, TX, January 29, 1991.

Bruno, T.J., Experimental Measurements on Trace Constituents in Natural Gas Condensates, Gas Research Institute Thermophysical Properties Contract Review Meeting, San Antonio, TX, March 14, 1991.

Bruno, T.J., Physicochemical Measurements on Trace Constituents in Natural Gas, Gas Research Institute Workshop, Chicago, IL, June 11-14, 1991.

Cezairliyan, A., Measurements of Properties of Materials at High Temperatures Under Rapid Heating Conditions, Workshop on Material Properties and Behavior under Ultrahigh Heating Rates, Alexandria, VA, August 2, 1991.

Chang, R.F., High Speed Pyrometry, Thermophysics Division Seminar, NIST, Gaithersburg, MD, December 17, 1990.

Defibaugh, D.R., Compressed Liquid Densities of R125 and R22, Thermophysics Division Seminar, NIST, Gaithersburg, MD, March 18, 1991.

Defibaugh, D.R., Compressed Liquid Densities of E134, Workshop on E134, NIST, Gaithersburg, MD, March 27, 1991.

Defibaugh, D.R., Compressed Liquid Densities of Pentafluoroethane, 11th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 26, 1991.

Diller, D.E., Measurements of the Viscosities of Saturated and Compressed Liquid Chlorodifluoromethane (R22), AIChE Meeting, Houston, TX, April 9, 1991.

Diller, D.E., Measurements of the Viscosities of Saturated and Compressed Liquid 1,1,1,2 Tetrafluoroethane (134a), 2,2, Dichloro-1,1,1 Trifluoroethane (R123), and 1,1-Dichloro-1-Fluoroethane (R141b), 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Dittmann, S., Performance of a Primary Vacuum Standard Down to 10^{-7} Pa, 37th National Symposium of the American Vacuum Society, Toronto, Canada, October 9, 1991.

Ehrlich, C.D., Recent Activities in the NIST Pressure Group, Division of Mechanical and Optical Metrology Colloquium, National Physical Laboratory, Teddington, England, May 23, 1991.

Ehrlich, C.D., Legal Metrology (Pertaining to Pressure Measurement) in the U.S., Ceskoslovensky Metrology Ustav (CSMU), Bratislava, Czechoslovakia, June 3, 1991.

Ehrlich, C.D., The Status of Piston Gage Metrology at NIST, Ceskoslovensky Metrologia Ustav (CSMU), Bratislava, Czechoslovakia, June 3, 1991.

Ely, J.F., Simulation of Systems with Large Size Ratios, Department of Chemical Engineering, University of AZ, November 27, 1990.

Ely, J.F., Transport Properties of Refrigerants, 11th Symposium on Thermophysical Properties, Boulder, CO, June 27, 1991.

Filippelli, A.R., Partial Pressure Analyzers of the Quadrupole Type--A Comparative Study of Several Different Commercial Instruments, 37th National Symposium of the American Vacuum Society, Toronto, Canada, October 9, 1990.

Filippelli, A.R., Performance Characteristics of Some Hot and Cold Cathode Ionization Gauges, Annual Symposium of the Delaware Valley Chapter of the American Vacuum Society, King of Prussia, PA, June 13, 1991.

Fox, J.R., Nonclassical Thermodynamic Description of Mixtures via Transformations of Classical Systems, 11th Symposium on Thermophysical Properties, Boulder, CO, June 27, 1991.

Friend, D.G., Thermodynamic Properties of the Methane-Ethane System, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Gillis, K.A., An All-Metal System for Measuring the Speed of Sound in Gaseous Refrigerants, 11th Symposium on Thermophysical Properties, Boulder, CO, June 24, 1991.

Gillis, K.A., Acoustic Measurements in Gases under Difficult Conditions, (Poster), Gordon Research Conference on the Chemistry and Physics of Liquids, Holderness School, Plymouth, NH, August 15, 1991.

Goodwin, A.R.H., Heat Capacities and Second Virial Coefficients of Methane Between 280 and 360 K Determined from Speed of Sound Measurements, 11th Symposium on Thermophysical Properties, Boulder, CO, June 27, 1991.

Goodwin, A.R.H., Thermophysical Properties of Gaseous Refrigerants from Speed of Sound Measurements: Results for 1,1,1,2-Tetrafluoroethane (R134a), 1-1, Dichloro-2,2,2-Trifluoroethane (R123), and 1,1-Dichloro-1-Fluoroethane (R141b), 11th Symposium on Thermophysical Properties, Boulder, CO, June 27, 1991.

Hanley, H.J.M., Neutron Scattering and Colloidal Suspensions, University of Bristol, London, England, April 23, 1991.

Hanley, H.J.M., Structure of Suspension Mixtures, 11th Symposium on Thermophysical Properties, Boulder, CO, June 24, 1991.

Hanley, H.J.M., Structure of Mixtures and Contrast Matching, Exxon, Annandale, NJ, July 18, 1991.

Hanley, H.J.M., Structure of Colloidal Suspensions, International Conference on Neutron Scattering, Oxford, England, August 27, 1991.

Haynes, W.M., Predictive Models for Low Temperature Properties of Air, 9th National Aero-Space Plane Technology Symposium, Orlando, FL, November 2, 1990.

Haynes, W.M., Thermophysical Properties of Fluids for the Gas Industry, Gas Research Institute Thermophysical Properties Contract Review Meeting, San Antonio, TX, March 14, 1991.

Haynes, W.M., Properties of Air, 10th National Aero-Space Plane Technology Symposium, Monterey, CA, April 25, 1991.

Huber, M.L., Thermal Conductivity and Thermal Diffusivity of Mixtures of Nitrogen, Oxygen, and Argon at Cryogenic Temperatures, AIChE Meeting, Houston, TX, April 10, 1991.

Huber, M.L., An Improved Corresponding States Model for the Prediction of Transport Properties of Fluids and Fluid Mixtures, AIChE Meeting, Houston, TX, April 10, 1991.

Huber, M.L., Prediction of Viscosity of Refrigerants and Refrigerant Mixtures, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Huber, M.L., Modeling of Supercritical Fluid Properties, Advanced Fuels Workshop, Wright-Patterson Air Force Base, Dayton, OH, September 5, 1991.

Jain, K., Characterization of a Piston Gage in Three Modes: Controlled Clearance, Simple, and Re-Entrant, Thermophysics Division Seminar, Gaithersburg, MD, February 25, 1991.

Looney, J.P., Low Density Measurements Using Optical Techniques, Thermophysics Division Seminar, NIST, Gaithersburg, MD, June 17, 1991.

MacDonald, R.A., Thermophysical Properties of Metals at High Temperatures, Physics Department Seminar, Towson State University, Towson, MD, November 27, 1990.

MacDonald, R.A., Analytical Method for Determining Thermal Conductivity from Dynamic Measurements, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Magee, J.W., High-Temperature Adiabatic Calorimeter for Constant Volume Heat Capacity Measurements of Compressed Gases and Liquids, Ninth Symposium on Energy Engineering Science, Argonne, IL, May 15, 1991.

Magee, J.W., Molar Heat Capacity at Constant Volume for Air from 67 to 300 K at Pressures to 35 MPa, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

McLinden, M.O., CFCs and the Search for Replacements, Colorado School of Mines, Golden, CO, October 23, 1990.

McLinden, M.O., Optimum Refrigerants for Non-Ideal Cycles, Chalmers University, Gothenburg, Sweden, November 16, 1990.

McLinden, M.O., Thermophysical Properties of R32 and R32 Mixtures, Workshop on R32, Washington, DC, March 19, 1991.

Miiller, A.P., Dynamic Thermophysical Measurements in Microgravity, Thermophysics Division Seminar, NIST, Gaithersburg, MD, February 4, 1991.

Miiller, A.P., Radiance Temperatures in the Wavelength Range 500-900 nm of Molybdenum at Its Melting Point, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Miiller, A.P., A Dynamic Technique for Measuring Thermal Conductivity at High Temperatures, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Moldover, M.R., Apparatus for Acoustic Measurements of Gases at High Temperatures, Ninth Symposium on Energy Engineering Sciences, Argonne, IL, May 15, 1991.

Moldover, M.R., Characterization of E245 at NIST, Workshop on E245, NIST, Gaithersburg, MD, May 29, 1991.

Morrison, G., Predicting Properties of Mixtures, Thermophysics Division Seminar, NIST, Gaithersburg, MD, January 28, 1991.

Morrison, G., Azeotropy in Refrigerant Mixtures, Thermal Machinery Group Seminar, NIST, Gaithersburg, MD, February 21, 1991.

Morrison, G., Ebulliometric Measurements of Alternative Refrigerants, Ninth Symposium on Energy Engineering Science, Argonne, IL, May 14, 1991.

Morrison, G., Azeotropes and Refrigerant Mixtures, 11th Symposium on Thermophysical Properties, Boulder, CO, June 27, 1991.

Morrison, G., Unlike Atom Interactions in Noble Gas Mixtures (Poster), Gordon Research Conference on the Chemistry and Physics of Liquids, Plymouth, NH, August 14, 1991.

Morrison, G., Azeotropy in Refrigerant Mixtures, Chambers Works of E.I. DuPont de Nemours Co., Deepwater, NJ, August 22, 1991.

Mountain, R.D., Approach to Stationary States, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Mountain, R.D., Computer Simulation Studies of Polarizable Water, 11th Symposium on Thermophysical Properties, Boulder, CO, June 26, 1991.

Mountain, R.D., Polarizable Water, Colorado School of Mines Seminar, Colorado School of Mines, Golden, CO, June 28, 1991.

Outcalt, S.L., Catalytic Cracking Detector, International Forum on Process Analytical Chemistry, Houston, TX, January 29, 1991.

Perkins, R.A., Thermal Conductivity and Viscosity Measurements of Fluids at High Temperatures, Ninth Symposium on Energy Engineering Science, Argonne, IL, May 15, 1991.

Perkins, R.A., Thermal Conductivity of R134a, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Perkins, R.A., Polarized Transient Hot Wire Thermal Conductivity Measurements, 11th Symposium on Thermophysical Properties, Boulder, CO, June 26, 1991.

Rainwater, J.C., Isothermal Phase Boundaries of Near-Critical Dilute Aqueous Salt Solutions, AIChE Meeting, Chicago, IL, November 12, 1990.

Rainwater, J.C., Correlation of Vapor-Liquid Equilibria of Ternary Mixtures in the Critical Region, AIChE Meeting, Chicago, IL, November 14, 1990.

Rainwater, J.C., The Modified Leung-Griffiths Model of Vapor-Liquid Equilibrium: Extended Scaling and Binary Mixtures of Dissimilar Fluids, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Rainwater, J.C., Theory of the Transport Properties of Moderately Dense Gases, 11th Symposium on Thermophysical Properties, Boulder, CO, June 26, 1991.

Ratnam, B.A., Damping of Ruchhardt Oscillations in Closed Ended Piston Gages, American Physical Society Meeting, Cincinnati, OH, March 18, 1991.

Ratnam, B.A., Experiments in Pressure Metrology, Physics Colloquium, Howard University, Washington, DC, April 17, 1991.

Ratnam, B.A., QC91: An Interactive Quality Assurance Program for Pressure Transfer Standards, Ruska Visitors Meeting, NIST, Gaithersburg, MD, April 12, 1991.

Ratnam, B.A., Piston Gage Metrology, NIST Piston Gage Course, NIST, Gaithersburg, MD, April 19, 1991.

Ripple, D., Forces Responsible for Wetting in C_7F_{14} + C_7H_{14} on Silicon, American Physical Society Meeting, Cincinnati, OH, March 20, 1991.

Rowley, R.L., Nonequilibrium Molecular Dynamics of Structured Molecules: Isomeric Effects on Viscosity of Butanes, AIChE Meeting, Chicago, IL, November 12, 1990.

Schmidt, J.W., Structure of Liquid Interfaces Using Ellipsometry, Department of Physics Colloquium, University of Delaware, Newark, DE, March 12, 1991.

Sengers, J.M.H. Levelt, Do Electrolyte Solutions Have Classical or Nonclassical Critical Behavior? AIChE Meeting, Chicago, IL, November 13, 1990.

Sengers, J.M.H. Levelt, Critical Behavior in Fluids and Fluid Mixtures, Department of Chemical Engineering, University of Virginia, Charlottesville, VA, March 21, 1991.

Sengers, J.M.H. Levelt, Myths and Facts about Supercritical Water, Thermophysics Division Seminar, NIST, Gaithersburg, MD, March 25, 1991.

Sengers, J.M.H. Levelt, The Peculiarities of Dilute Near-Critical Mixtures, Department of Chemical Engineering, University of Maine, Orono, ME, April 5, 1991.

Sengers, J.M.H. Levelt, Solubility Near the Solvent's Critical Point, 2nd International Symposium on Supercritical Fluids, Boston, MA, May 21, 1991.

Sengers, J.M.H. Levelt, Standard States, Reference States, and Finite-Concentration Effects in Near-Critical Aqueous Solutions, 11th Symposium on Thermophysical Properties, Boulder, CO, June 25, 1991.

Sengers, J.M.H. Levelt, Critical Behavior of Ionic Fluids: An Experimental Assessment, Gordon Research Conference on the Chemistry and Physics of Liquids, Plymouth, NH, August 12, 1991.

Tilford, C.R., Design of Vacuum Calibration Systems, 37th National Symposium of the American Vacuum Society, Toronto, Canada, October 9, 1990.

Tilford, C.R., Performance of a Primary Vacuum Standard Down to 10^{-7} Pa, 37th National Symposium of the American Vacuum Society, Toronto, Canada, October 9, 1990.

Tilford, C.R., Vacuum Standards and Calibrations, Annual Symposium of the Delaware Valley Chapter of the American Vacuum Society, King of Prussia, PA, June 13, 1991.

Tison, S., The S&L Crisis, Leak Rate Measurements, and the Physics of Exponential Phenomena, Thermophysics Division Seminar, NIST, Gaithersburg, MD, April 8, 1991.

Van Poolen, L.J., Determination of Critical Densities from Coexisting Density Measurements: Application to Refrigerants R22, R134a, and R124, 11th Symposium on Thermophysical Properties, Boulder, CO, June 26, 1991.

Weber, L.A., Ebulliometric Measurement of the Vapor Pressures of R123 and R141b, 11th Symposium on Thermophysical Properties, Boulder, CO, June 26, 1991.

Weber, L.A., PVT and Thermodynamic Properties of R141b in the Gas Phase, XVIIIth International Congress of Refrigeration, Montreal, Canada, August 14, 1991.

Welch, B.E., Reduction of Gas Piston Gage Uncertainties, Thermophysics Division Seminar, NIST, Gaithersburg, MD, March 11, 1991.

3. Patent Awards and Applications

Bruno, T.J., Separator Solvator for Supercritical Fluid Extraction (Granted), Apparatus and Method for Evaporative Sample Concentration (Submitted)

Moldover, M.R., Improved Oscillating Tube Densimeter (Submitted)

Morrison, G., Azeotropic Mixtures as Alternative Refrigerants (Submitted)

4. Committee Assignments

T.J. Bruno
NIST Boulder Laboratories Library Advisory Committee
NIST Shops Advisory Committee
NIST Research Advisory Committee

A. Cezairliyan
International Organizing Committee, European Thermophysical Properties Conference
ASME K-7 Thermophysical Properties Committee
International Thermophysics Congress (Chairman)
International Commission on Standardization of Thermophysical Measurement Technique
ASTM Thermophysical Properties Subcommittee
Governing Board of the International Thermal Expansion Conference
Touloukian Award Subcommittee of the ASME Heat Transfer Division (Chairman)
International Organizing Committee of the Subsecond Thermophysics Workshops

S. Dittmann
AVS Vacuum Technology Division (Board of Directors)

C.D. Ehrlich
BIMP Consultative Committee for Mass and Related Quantities, Working Groups on High Pressure and Medium Pressure
ASTM Committee E07 on Nondestructive Testing
ASTM Subcommittee E07.08 on Leak Testing
AVS Leak Testing Subcommittee (Co-Chairman)
NCSL Recommended Practices Committee on Deadweight Pressure Standards (Chairman)

J.F. Ely
- ASME K-7 Thermophysical Properties Committee
- GPA Databook Revision Committee
- Boulder Computer Users Group
- NIST Supercomputer Source Evaluation Board

A.R. Filippelli
- AVS Vacuum Technology Division (Board of Directors)
- AVS Recommended Practices Committee on the Calibration of Mass Spectrometers for Partial Pressure Analysis
- Journal of Vacuum Science and Technology Shop Note Award Committee (Chairman)

J.S. Gallagher
- International Association for Properties of Water and Steam, Working Group for Thermophysical Properties
- ASME Research and Technology Committee on Water in Thermal Power Systems
- ASME Research Subcommittee on the Properties of Water and Steam (Secretary)

H.J.M. Hanley
- ASME K-7 Thermophysical Properties Committee

W.M. Haynes
- International Energy Agency Annex 18 - Thermophysical Properties of Environmentally Acceptable Refrigerants
- ASTM Committee D03 on Gaseous Fuels

M.A. Huber
- Boulder Computer Users Group
- Boulder Editorial Review Board

R.W. Hyland
- AVS Recommended Practices Committee on the Use of Capacitance Diaphragm Gages

R.F. Kayser
- Working Group on Mitigation and Adaptation Research Strategies, Committee on Earth and Environmental Sciences, Federal Coordinating Council for Science, Engineering, and Technology (FCCSET)
- Interdepartmental Task Force on Environment and Competitiveness

J.P. Looney
- CSTL Colloquium Committee

R.A. MacDonald
- NIST Employee Advisory Committee for the Personnel Management Demonstration Project (Chairman)
- Washington Editorial Review Board

M.O. McLinden

ASHRAE Technical Committee 3.1 - Refrigerants and Brines (Chairman)
ASHRAE Standard Project Committee 34 - Nomenclature and Safety Classification of Refrigerants
International Energy Agency Annex 18 - Thermophysical Properties of Environmentally Acceptable Refrigerants (Operating Agent/Chairman)

A.P. Miiller

ASME K-7 Thermophysical Properties Committee
ASTM Committee E37 on Thermal Measurements
ASTM Thermophysical Properties Subcommittee
Touloukian Award Subcommittee of the ASME Heat Transfer Division

M.R. Moldover

Metals and Alloys Containerless Processing, NASA Proposal Review Panel

G. Morrison

AIChE Design Institute for Property Prediction (DIPPR), Project 802

R.D. Mountain

NIST Library Subject Specialist Committee
NIST Users Committee for Scientific Computing (Chairman)

J.M.H. Levelt Sengers

International Association for Properties of Water and Steam (President and U.S. National Delegate)
International Association for Properties of Water and Steam, Working Group for Thermophysical Properties
ASME Research Committee on the Properties of Water and Steam

J.V. Sengers

ASME K-7 Thermophysical Properties Committee
ASME Research Committee on the Properties of Water and Steam
International Association for Properties of Water and Steam, Working Group for Thermophysical Properties
International Thermophysics Congress
Touloukian Award Subcommittee of the ASME Heat Transfer Division

C.R. Tilford

Radio and Technical Commission for Aeronautics, Special Committee 150, Performance Requirements for 100 Foot Vertical Separation of Aircraft Above Flight Level 290
BIPM Consultative Committee for Mass and Related Quantities, Medium and Low Pressure Working Groups (Chairman)

S.A. Tison

ASTM Subcommittee E07.08 on Leak Testing (Vice Chairman)

5. Other

a. Editorships

T.J. Bruno

Book, Supercritical Fluid Technology: Reviews in Modern Theory and Applications, Two Volumes, CRC Press (Co-Editor)

A. Cezairliyan

Compendium on Thermophysical Properties Measurement Methods, Plenum Publishing Company (Editor)
International Journal of Thermophysics (Editor-in-Chief)
Journal of High Temperature Science (Editorial Board)
High Temperatures-High Pressures (Editorial Board)

J.F. Ely

Fluid Phase Equilibria (Editor)
Book, Supercritical Fluid Technology: Reviews in Modern Theory and Applications, Two Volumes, CRC Press (Co-Editor)
Society of Petroleum Engineers Phase Behavior Monograph (Editorial Board)

b. Conferences/Workshops Sponsored/Co-Sponsored

11th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO

c. Faculty Appointments

T.J. Bruno

Adjunct Associate Professor, Department of Chemical Engineering and Petroleum Refining, Colorado School of Mines, Golden, CO

H.J.M. Hanley

Adjunct Professor, Department of Chemical Engineering, University of Colorado, Boulder, CO

J.F. Ely

Adjunct Professor, Department of Chemical Engineering and Petroleum Refining, Colorado School of Mines, Golden, CO

J.C. Rainwater

Adjunct Professor, Department of Physics, University of Colorado, Boulder, CO

d. SRD Activities

SUPERTRAPP, Upgrade
REFPROP, Updated